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NAS9-16009

Formulation and Characterization of Polyimide Resilient Foams of Various Densities for Aircraft Seating Applications

Final Report
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SUMMARY

The following paragraphs contain a summary of the significant accomplishments generated during the course of the contract effort.

- The task dealing with Foam Fabrication Studies has resulted in a microwave foaming and curing process, using the 15 kW (GFE) microwave oven, which has consistently produced foams with uniformity of physical properties within and between buns.

- The values of the density and ILD of the foams were found to be directly related to the outlet temperature of the spray dryer. The lowest values of ILD were obtained at an outlet temperature of 56-60°C (132.8-140°F)

- The effort of the same task proved the feasibility of foaming polyimide powder precursors in an open mold and provided a method to overcome foam collapse, a major deficiency of the free-rise foaming process.

- A rectangular polypropylene open mold configuration modified with a bottom grid, corner vents and insulated with polyimide foam liners was selected for all the experiments carried out during the course of this program.

- The task dealing with Formulation and Optimization has resulted in the selection of a blowing agent to promote a more uniform foam rise during microwave foaming.

- The ILD values of the polyimide foams are independent of the aliphatic diamine ratio over the range reported and no classification into groups is attainable.

- The study of compositional ratios has resulted in an improved precursor composition made at a ratio of 0.30:0.54:0.16 moles of heterocyclic diamine, aromatic diamine and aliphatic diamine, respectively, per mole of BTDA.

- Three parameters have emerged from Task II as most critical in classifying foams into groups according to ILD values. These are: outlet temperature, concentration of the blowing agent and power ratio.

- The efforts of Task III have resulted in the selection of optimized foaming parameters which produced finished product with homogeneous property distribution within and between buns.

- Processing and compositional parameters have been identified which regulate the ILD values of the foams and provide methods to classify the foams according to established ILD values at 25 percent deflection. These important parameters are:

  - The outlet temperature
  - Concentration of the blowing agent
  - Crushing techniques

- During the execution of Task IV efforts, dealing with foam evaluation and classification, these important parameters have been fully evaluated to achieve foam classification.

- The ILD values of polyimide foams at 25 percent deflection are directly proportional to the outlet temperature and inversely proportional to the concentration of the blowing agent.

- Powder precursors spray dried at an outlet temperature of 69±1°C (156.2°F) produce foams with ILD values falling within three of the five classes established for the program, specifically Class III, Class IV and Class V foams by variation of the blowing agent concentration within clearly defined values.

- Foams produced from powder precursors spray dried at the selected outlet temperature of 68-70°C (154.4-158.0°F) possess the best fatigue properties and homogeneity within and between buns.

- Foam crushing techniques in combination with high concentration of the blowing agent were employed to produce Class I and Class II foams.

- The process parameters and compositions employed to produce the five classes of foams have been presented in this task.

- The minimum functional and performance requirements for each of the five classes identified have been established and final product specifications written.

- Prototype production samples for each of the five classes were produced using the process conditions selected in this program. These samples have been submitted to NASA-Johnson Space Center for evaluation in seating applications.

1

PROGRAM SCOPE AND OBJECTIVES

The principal objective of this program is to formulate, fabricate and characterize polyimide foams in order to establish five classes of foams selected in accordance with the following ILD values at 25 percent deflection.

Class	ILD at 25% Deflection
1	18
2	24
3	44
4	50-55
5	70-80

Unlike conventional cellular materials, the polyimide foams under study in this program combine three important attributes:

1. Inherent non-burning characteristics.

2. No detectable smoke formation.

3. No incapacitating cabin environments.

The program consists of six major tasks which define the objectives and the work content. The work plan constituting the various objectives and their milestones is shown in Figure 1.

The fabrication techniques used in this program are those reported in previous NASA-JSC funded programs (Refs 1, 2, and 3), and those developed through the continual effort reported in this document. The compositions studied are based on a technology previously developed by International Harvester with efforts leading to the selection of the five groups of polyimide foams which have been clearly identified on the basis of established ILD values, seating comfort and durability.

The effort starts with studies of optimization of the foaming and curing processes to yield uniformity within and between buns. This task is followed by compositional studies directed to achieve foams with predetermined ILD values. The task continues with optimization and characterization of the selected candidates for final classification into five groups and for fabrication of final prototypes for submittal to NASA-JSC.

A final task dealing with Reporting and Coordination covers the effort necessary to report the program status and includes a mid-term and final presentation to acquaint NASA-JSC with the progress of the program.

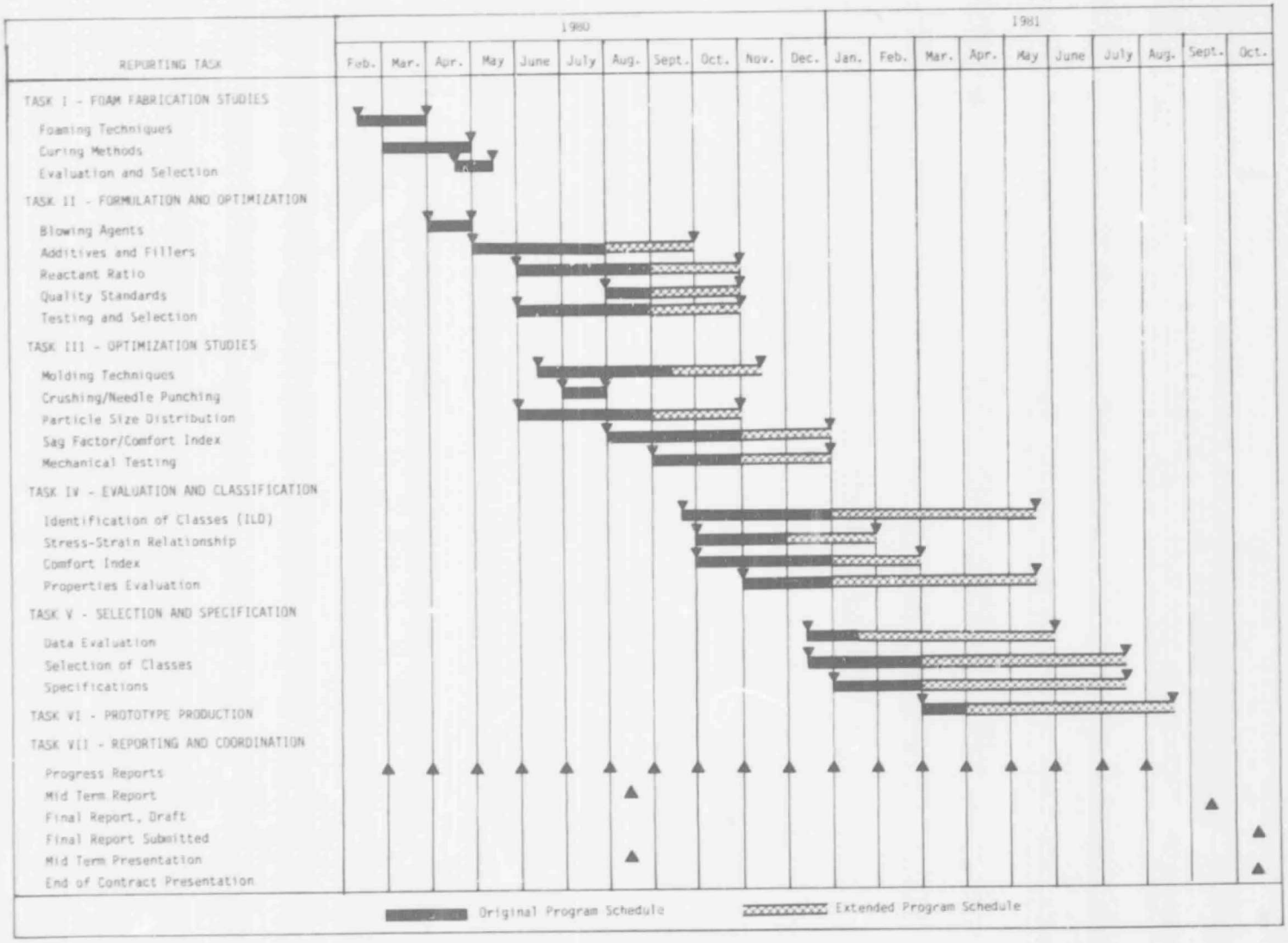


Figure 1. Program Schedule

The overall technical content of the program was scheduled to cover a period of twelve months and included an additional two months for final draft preparation and submittal. A five months extension of the period of performance was requested and the extension approved by NASA-JSC. This extension was necessary to satisfy the high demand of polyimide materials for a variety of NASA-JSC sponsored projects.

2

BACKGROUND AND PROGRAM APPROACH

International Harvester has developed the basic technology for formulating light weight, heat- and fire-resistant low smoke-generating polymers for containment of fuel fires. This technology is based on polyimide chemistry.

A significant effort has already been devoted to optimize this technology in three previous programs funded by NASA-JSC. In the first program (Ref. 1), the major deficiencies of the polyimide flexible resilient foams were identified, namely fatigue strength, resistance to high humidity, and production cost. The major emphasis of the second and third programs (Refs. 2 and 3) resulted in significant improvement of foam properties as they relate to hydrolytic stability, fatigue resistance, and cost. In addition, other types of polyimide materials were investigated resulting in the production of advanced hardware and products. The products included, in addition to the flexible resilient foams, thermal acoustical insulation, floor paneling, wall paneling and molded shapes.

The properties demonstrated by these products represent a technological advancement in the art of polyimide development, processing and fabrication. Additional effort has been carried out during the course of this program to upgrade and classify the flexible material into groups for fabrication of cushions possessing acceptable comfort properties. This work has been directed toward refinement and selection of foaming processes using a variety of previously developed foaming techniques and definition of property relationships to arrive at the selection and classification of polyimide foams into five groups in accordance with predetermined ILD values. The formulation and processes to produce the powder precursors and to fabricate the foams have been those developed in NAS 9-15484 (Ref. 3) with additional work directed to achieve foams with improved cushioning properties. Candidate materials have been selected, characterized and five classes of flexible foams established in accordance with predetermined ILD values at 25 percent deflection.

3

EXPERIMENTAL PROCEDURES

This section outlines the experimental procedures and includes selection of raw materials (Sec. 3.1), synthesis of the liquid and powder polyimide precursors (Sec. 3.2), fabrication of the flexible forms and test procedures (Sec. 3.3), and chemical reactions (Sec. 3.4).

3.1 SELECTION OF RAW MATERIALS

The raw materials used in the preparation of the precursors studied in this program are those claimed in one or more of International Harvester's existing patents. The diamines, dianhydrides, chemicals and additives used in this program and their relevant physical properties are listed below.

- Benzophenone 3,3',4,4' Tetracarboxylic acid dianhydride - This product was obtained from the Gulf Oil Co., Chemical Division. The off-white material was slurried in warm acetone containing four percent dimethylformamide and dried at 120°C (248°F) to yield a material (MP 225-226°C, 437-439.5°F) suitable for synthesis of polyimide precursors.

- Pyromellitic Dianhydride - This product was obtained from Aldrich Chemicals (MP 283-286°C; 541-547°F) and used without purification.

- 2,6 Diaminopyridine - This highly purified diamine (MP 120-122°C; 248-252°F) was obtained from Wall Chemicals and used without purification.

- Methylene dianiline - This commercial grade diamine (MP 90-92°C, 194-197.6°F) was obtained from Allied Chemicals Co. and used without purification.

- Para phenylene diamine (MP 138-143°C; 280-289°F) was purchased from Aldrich Chemicals and used without purification.

- Meta phenylene diamine - This commercial grade diamine was obtained from Miller-Stephenson Chemical Co. and used without purification (MP 62-63°C; 143.6-145.4°F).

- 1,6 Diaminohexane - This commercial grade aliphatic diamine (MP 39-40°C, 102-104°F) was obtained from the Celanese Chemical Company and used without purification.

- Methyl Alcohol, Ethyl Alcohol, Propyl Alcohol - These commercial grade solvents were purchased locally from Atlas Chemical Company and used as received.

- Surfactants AS-2 and Zonyl were obtained from E.I. Dupont de Nemours.

- L Type surfactants were purchased from Union Carbide.

- The blowing agents were purchased from Uniroyal and Stepan Chemical Company.

- All other inorganic and organic additives were purchased from Aldrich Chemicals.

The analysis of the major raw material by Infrared Spectroscopy, obtained by the KBr pressed wafer method on a Beckman Model IR 8 grating infrared spectrophotometer, is shown:

- Benzophenone 3,3',4,4' Tetracarboxylic acid dianhydride unpurified (Fig. 2), and purified (Fig. 3). Note the reduction of the peak at 3500 cm^{-1} for the free carboxylic groups and improved resolution of the purified material.

3.2 SYNTHESIS OF THE LIQUID AND POWDER PRECURSORS

The following procedures are typical of those used to prepare the polyimide precursors.

3.2.1 Monomeric Terpolyimide Liquid Precursors

The dianhydrides were added to 240 ml of alcohol in a one-liter, three neck flask, equipped with thermometer, mechanical stirrer and reflux condenser. After addition, the mixture was heated to reflux.

The mixture was then refluxed for 60 minutes to ensure complete esterification. It was then cooled to 25-35°C (77-95°F). The diamines were added to this mixture slowly so that the reaction temperature did not exceed 65°C (149°F). Alcohol, based on the dilution ratio required, was added at this stage along with additives, if any.

The 55 liter reactor for the preparation of liquid precursors in large lots is shown in Figure 4. The bench scale arrangement located in the laboratory is shown in Figure 5.

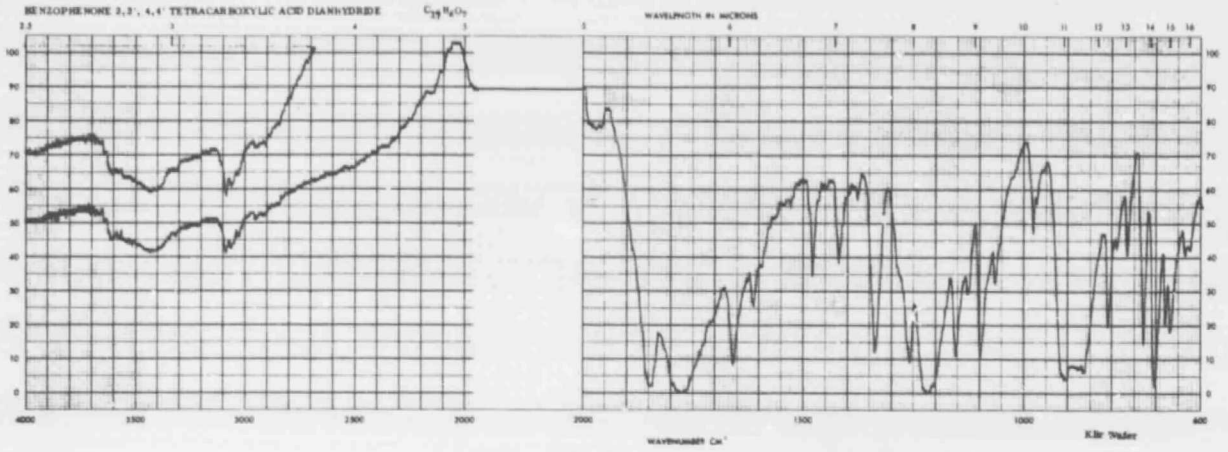


Figure 2. IR Spectrum of Benzophenone 3,3',4,4' Tetracarboxylic Acid Dianhydride

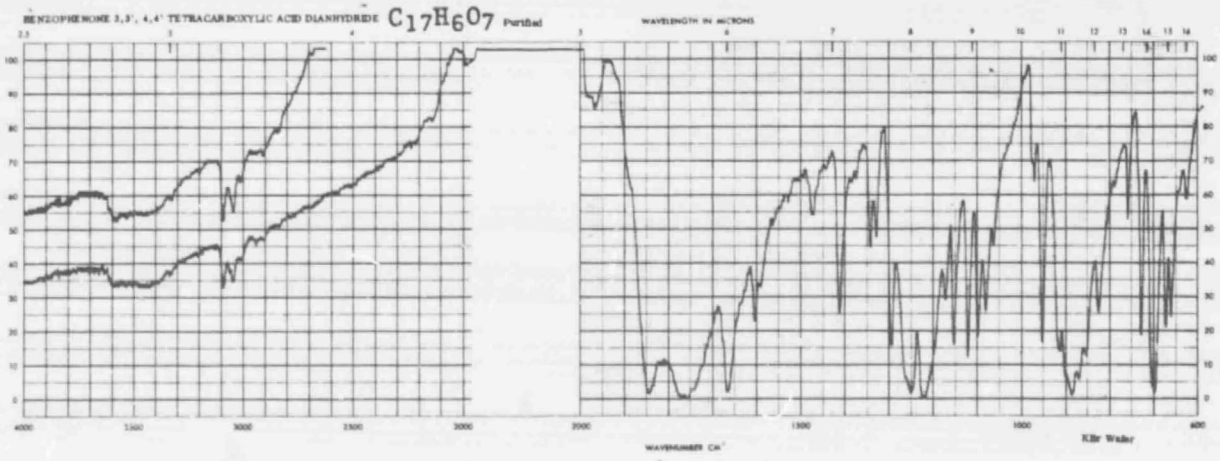


Figure 3. IR Spectrum of Benzophenone 3,3',4,4' Tetracarboxyic Acid Dianhydride

3.2.2 Monomeric Terpolyimide Powder Precursors

The procedure used to prepare the powder precursors from the liquid resins is based on a spray drying process.

The liquid resin to be dried was first diluted with alcohol (30 phr) and the feed was started into the atomizer and manually adjusted throughout the operation to maintain the outlet temperature in the desired range. The powder was collected in a five gallon plastic jar mounted under the cyclone separator. A Niro Mobile Minor Spray Dryer was used in this process which is shown in Figure 6. This unit was modified to permit use of inert gas as a drying medium.

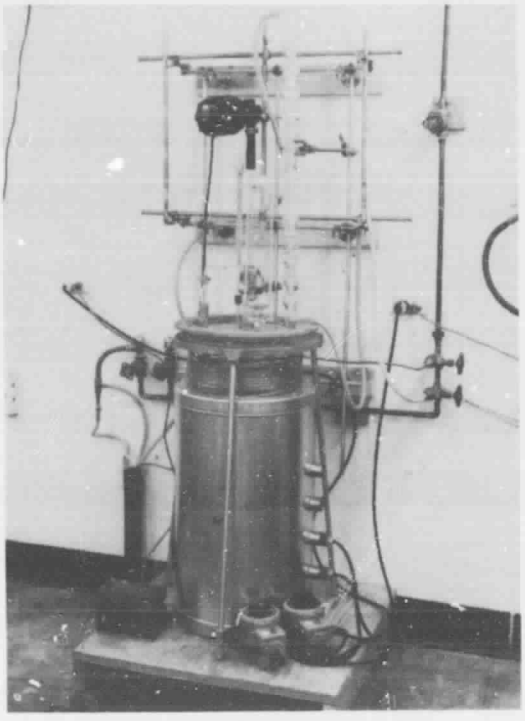


Figure 4.

55 Liter Reactor for the Preparation of Polyimide Liquid Resins

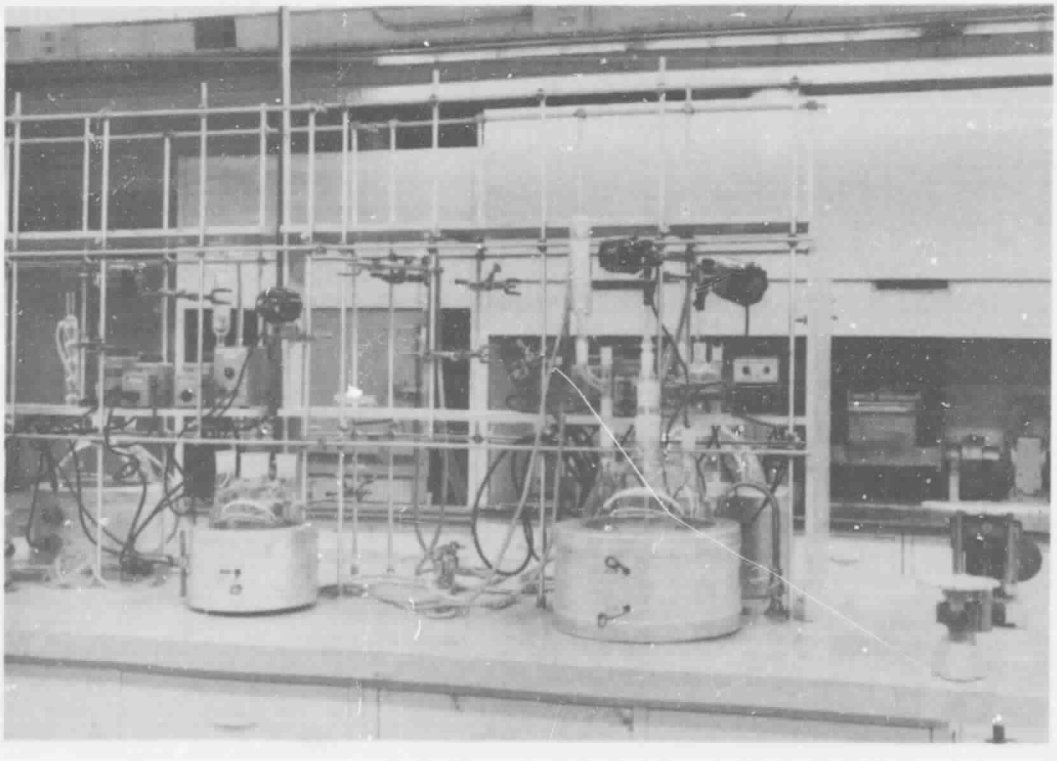


Figure 5. Bench-Scale Arrangement for the Preparation of Liquid Resins

Figure 6.

Niro Mobile Minor Spray Dryer

3.3 FLEXIBLE RESILIENT FOAMS FROM THE TERPOLYIMIDE POWDER PRECURSORS

The foams were produced by microwave foaming processes using a Gerling Moore 5 kW Batch Cavity Model 4115 (Figure 7) for small experimental foams and the 15 kW GFE unit (Figure 8) for larger size foams. Both microwave ovens operate at a frequency of 2450 MHz.

The 15 kW GFE microwave oven was installed in the Research Pilot Plant facility shown in Figure 9. Figure 10 shows an electrically heated circulating oven for curing the foams by thermal methods. This oven is equipped with a moveable cart to carry large foam slabs from the microwave oven into the thermal oven for the curing process. The two ovens are installed in series for ease of operation.

To make a foam, the powder precursor was laid on a sheet of Teflon coated glass fabric and both placed in the microwave oven at room temperature. Occasionally the powder was preheated to accelerate the foaming process. After a period of exposure to the high frequency radiation the powder expanded to a homogeneous cellular material which was further processed in the microwave oven to achieve complete condensation reaction and curing. The curing process was occasionally carried out by thermal methods and involved heating the expanded mass in an electrically heated oven shown in Figure 10.

Both free-rise and constrained foaming methods were used. The free-rise method involved microwave heating the powder precursor and permitting the foam to expand freely which often resulted in irregular shapes.

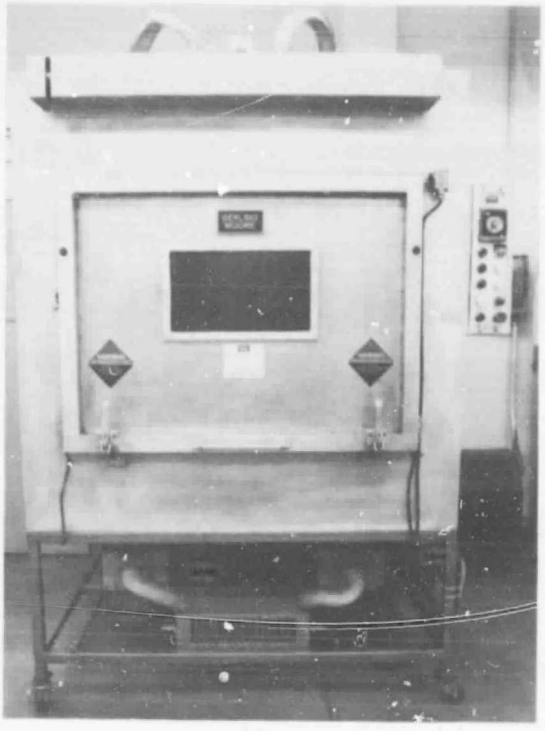


Figure 7.

Gerling Moore 5 kW Microwave Oven
Model 4115

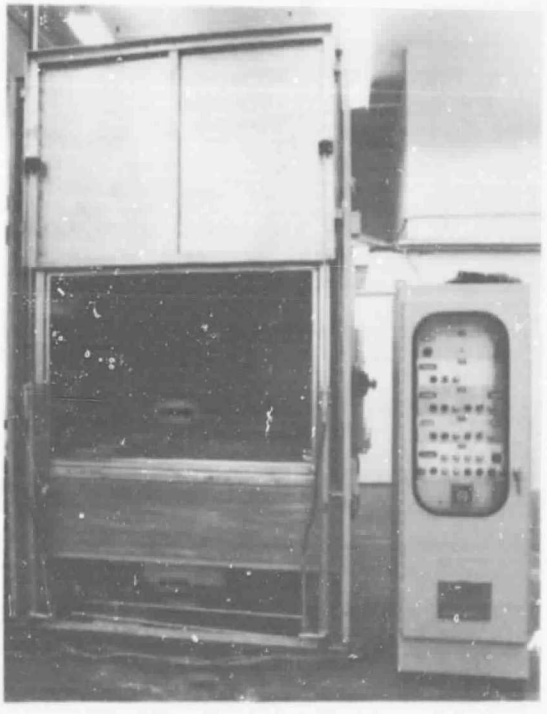


Figure 8.

15 kW Microwave Oven (GFE)

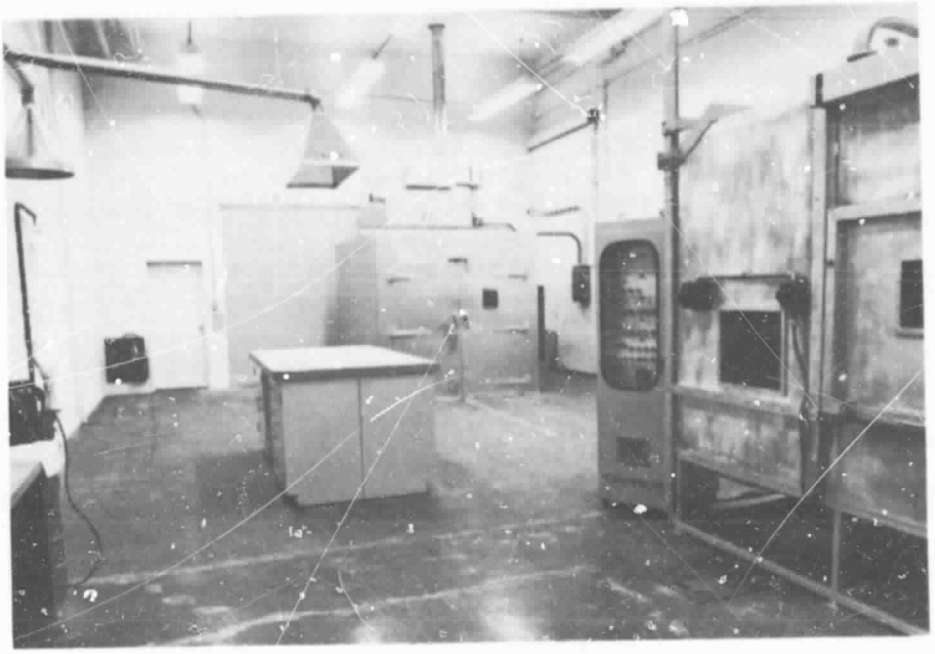


Figure 9. Research Pilot Plant Facility

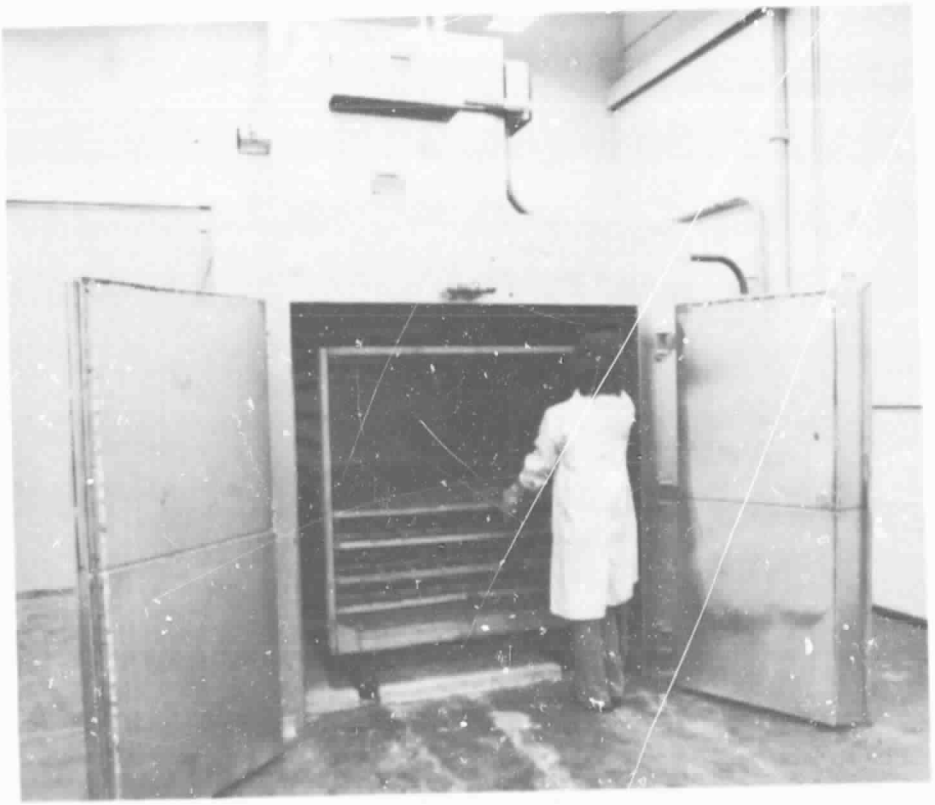


Figure 10. Electrically Heated Circulating Oven (Despatch)

The constrained foaming method was carried out by placing the powder precursor into a microwave compatible mold and allowing the foam to conform to the shape of the mold. A polypropylene mold, 61 x 91.5 x 40.5 cm (24 x 36 x 16 in.) is shown in Figure 11.

The fully cured foams were cut to the desired shape in a vertical band knife shown in Figure 12 and flexibilized by passing the foam slabs between two rotating steel rollers which compressed the foam resulting in increased softness and resilience. The flexibilizer is shown in Figure 13. Samples of finished flexible, resilient foam are shown in Figure 14.

Each foam was tested for the most critical properties set forth in the plan of performance. The critical properties are briefly reviewed below.

The compression set of the foams at 50 and 90 percent compression was determined according to ASTM Designation D-3574-77, using two steel plates held parallel to each other by clamps and the space between the plates adjusted to the required thickness by means of spacers. This method was modified during the execution of this program by compressing the foams at 30 and 70 percent compression respectively to compensate for the higher resistance of polyimide foams to compressive forces.

The resistance of the foam to cyclic shear-loadings (fatigue test) was determined in accordance with ASTM Designation D-3574-77, Procedure A, with the

Figure 11. Polypropylene Mold

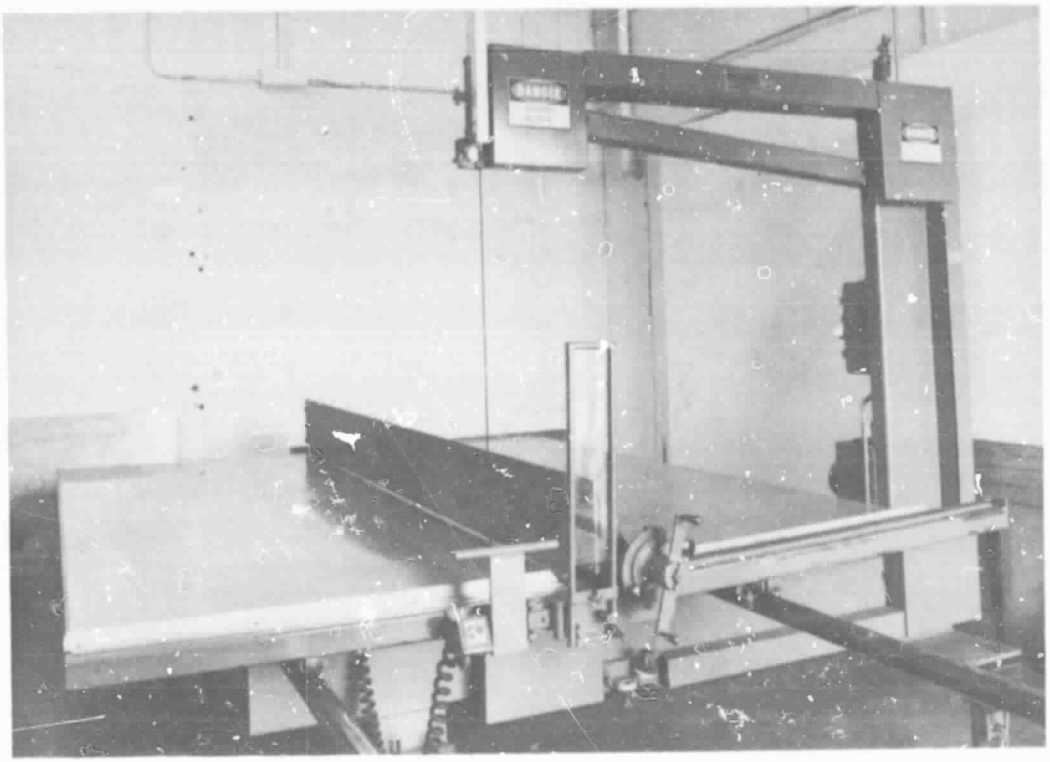


Figure 12. Femco Vertical Band Knife

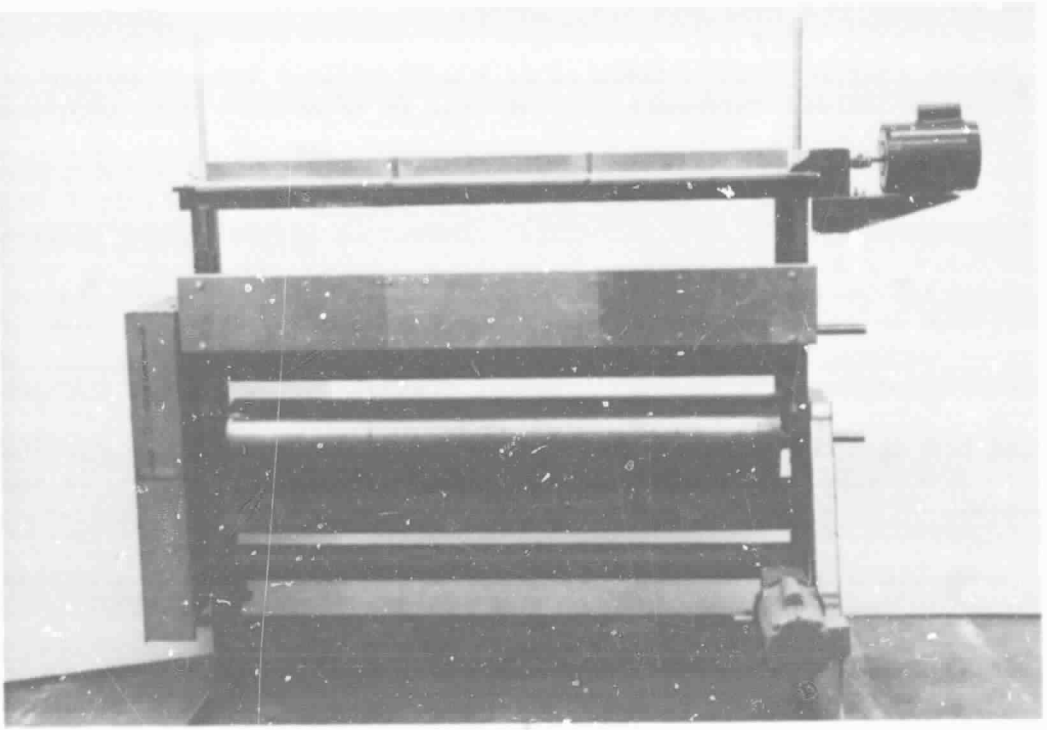


Figure 13. Foam Flexibilizer

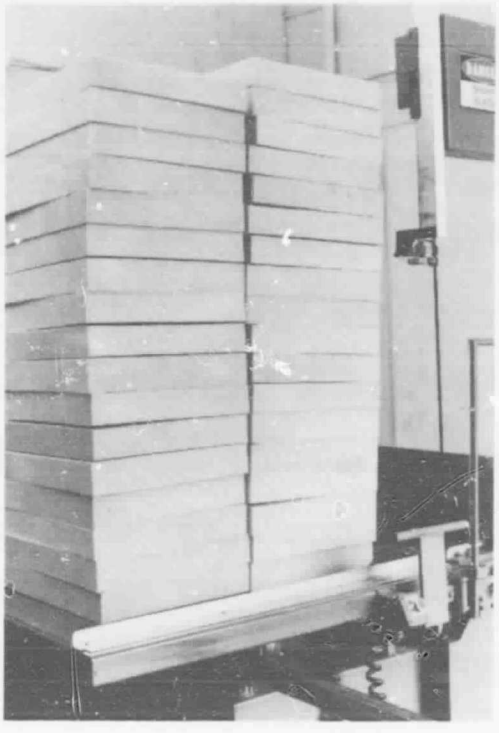


Figure 14.

Flexibile, Resilient Foams Cut to Size

exception that examination and measurement of the foam for loss of thickness was made at 8,000 and 20,000 cycles. The fatigue tester was constructed in accordance with the same ASTM Designation.

Indentation load deflection tests at 25 and 65 percent deflection were carried out using an Instron Universal Test Machine in accordance with ASTM Designation D-3574-77.

Humidity tests were carried out in a vapor-temperature Controlled Relative Humidity Chamber. This is a mechanical convection controlled humidity tester manufactured by Blue M Company. Using this chamber, foam samples were subjected to 100 percent relative humidity at a dry bulb temperature of 74°C (165°F) for a period of seven days. Performance of the test samples was evaluated qualitatively by embrittlement or degradation of the cellular structure and quantitatively by ball rebound resiliency method and ILD changes.

Testing for other mechanical properties was done according to the standard methods of testing slab flexible urethane foams described in ASTM designation D-3574-77.

The flammability characteristics of the foams were obtained by determination of the smoke density in accordance with the NBS procedure utilizing the NBS Smoke Density Chamber (Ref. American Instrument Co., Aminco Catalog No. 4-5800, Intruction No. 941). The NBS Smoke Density Chamber is shown in Figure 15. The relative flammability of the foams was determined by measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that would just support combustion of the material (LOI). The test apparatus

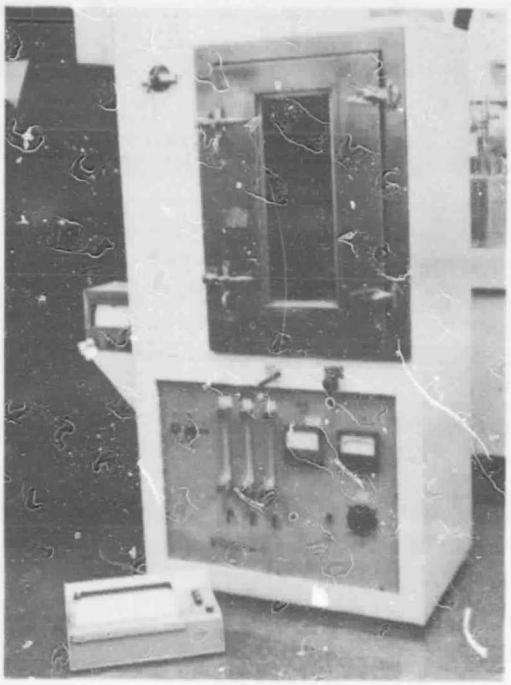


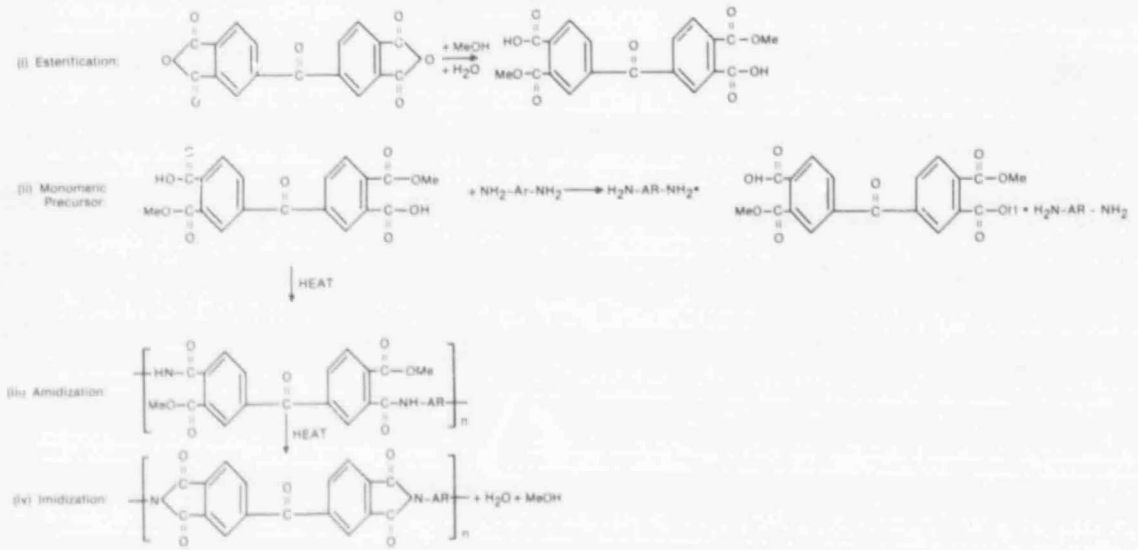
Figure 15.

NBS Smoke Density Chamber

for this determination was prepared in accordance with ASTM Designation D-2863.

3.4 CHEMICAL REACTIONS

The reactions that occur during the synthesis of the liquid and powder resins and subsequent foaming are too complex to be fully described here. The general model is presented below:



Briefly, the tetracarboxylic acid dianhydrides are first esterified to yield a diester (i) which by addition of diamines produces a monomeric liquid precursor (ii). The powder monomeric precursor is a self reacting monomer which at 149-204°C (300-400°F) produces a polyamic ester and expands into a low density cellular structure (iii). The final condensation reaction (iv) occurs at 260-315°C (500-600°F) where complete imidization takes place with formation of a high molecular weight polyimide structure.

The determination of the molecular weight equivalent of the powder precursor has been done using a diazo type titration with external indicator. Results indicate a chain length of about 20-30 molecules, equivalent to a molecular weight of approximately 10,000 to 15,000.

Infrared Spectroscopy was used to follow the progress of the reactions of imidization. Precursors and foams were made into powders which were then used to make KBr wafers. These were then analyzed on a Beckman Model IR 8 grating spectrophotometer. The disappearance of the primary amino group bands from 3300 cm^{-1} to 3500 cm^{-1} as the polymerization proceeds from precursor (Figure 16) to uncured foam (Figure 17) to cured foam (Figure 18), indicated that the nitrogens are reacting to form imide bonds. In addition, the amide peak at 1675 cm^{-1} which is very strong in the precursor (Figure 16), weaker in the uncured foam (Figure 17) and weakest in the cured foam (Figure 18) also indicates that the imide bond is being formed. The amide peak does not totally disappear due to the presence of a ketone peak in the same region. Finally, the presence of bands at 1785 cm^{-1}, 1725 cm^{-1}, and 720 cm^{-1} (Figures 17, 18 and 19) definitely indicates the formation of the imide bonds. A 20 minute cure time is shown to be sufficient by comparing Figures 18 and 19 and noticing the lack of visible change despite the additional 70 minutes of curing time.

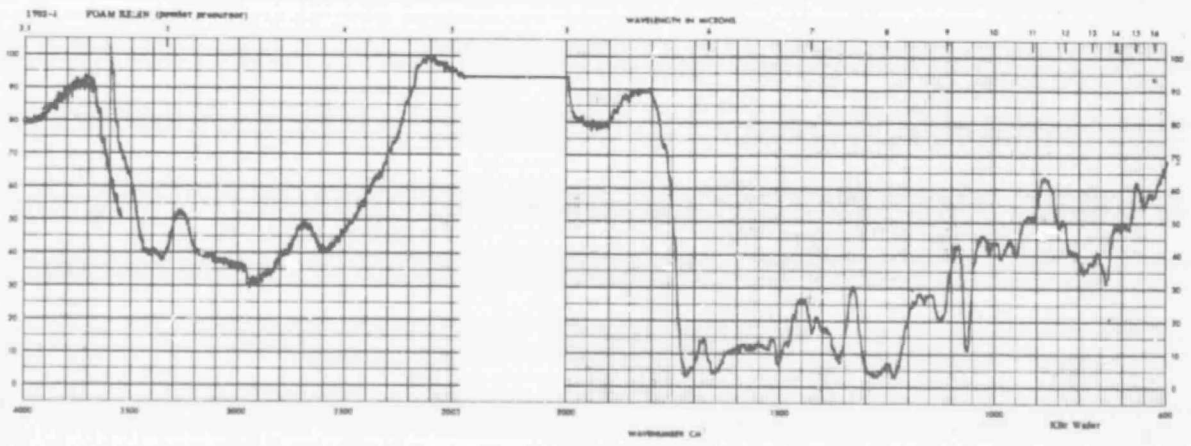


Figure 16. IR Spectrum of 1702-1 Foam Resin (Powder Precursor)

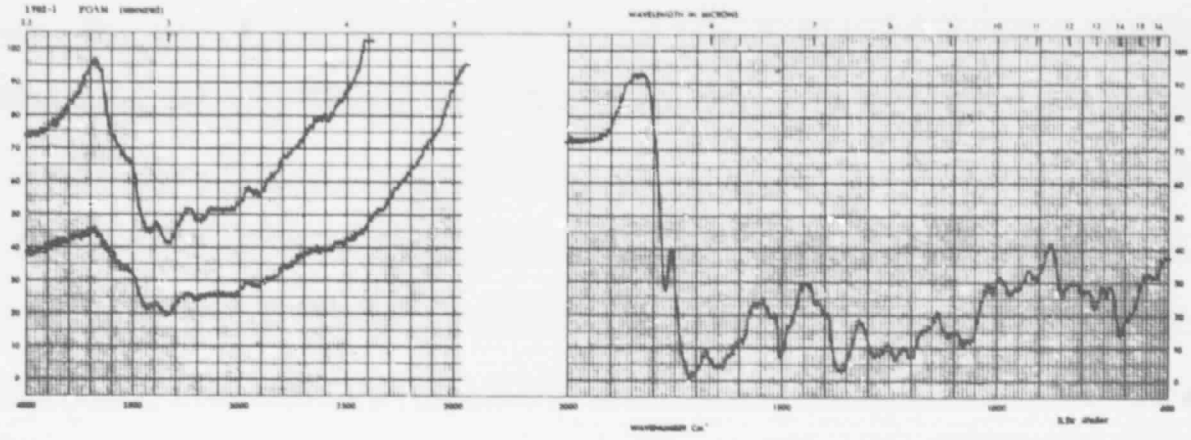


Figure 17. IR Spectrum of 1702-1 Foam (Uncured)

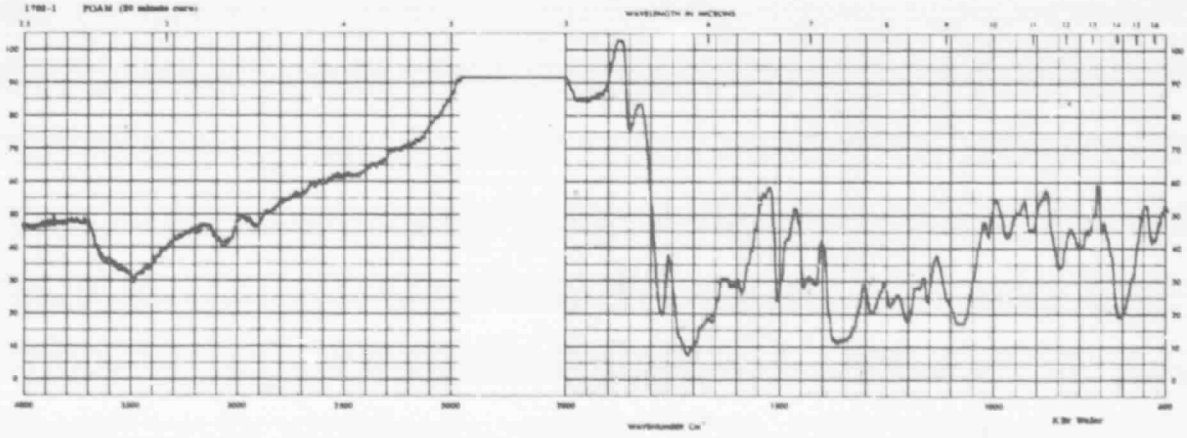


Figure 18. IR Spectrum of 1702-1 Foam (20 Minute Cure)

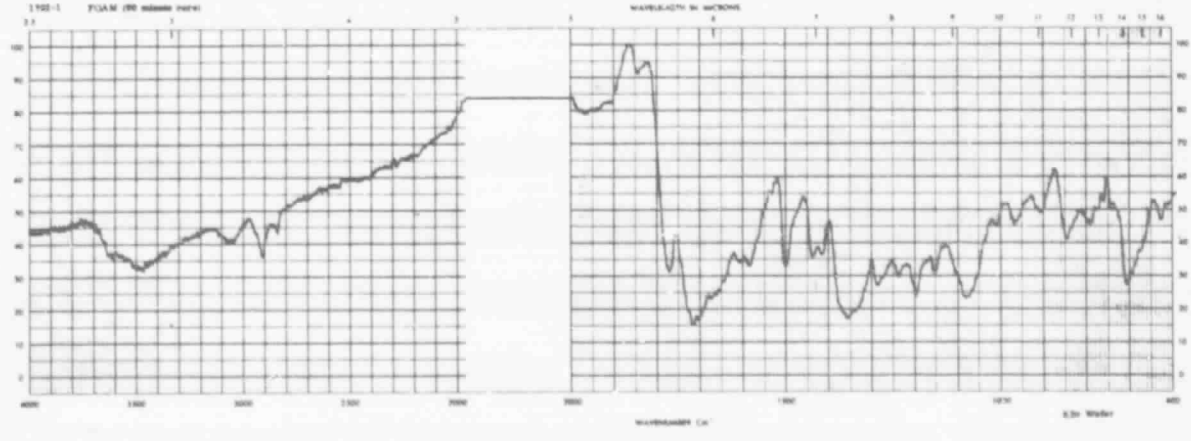


Figure 19. IR Spectrum of 1702-1 Foam (90 Minute Cure)

4

EXPERIMENTAL RESULTS

This section describes the experimental effort carried out during the period of performance and is divided into six major tasks to improve clarity.

The first task (4.1) covers evaluation of fabrication techniques to achieve uniformity of foam properties followed by two major tasks (4.2 and 4.3) covering optimization of precursor compositions and processing parameters, respectively. The next major task (4.4) covers the study leading to the classification of the foams into five different classes according to predetermined ILD values at 25 percent deflection followed by final selection (4.5) and preparation of prototype foams for evaluation in commercial aircraft (4.6).

4.1 TASK I - FOAM FABRICATION STUDIES

The effort of this task starts with studies leading to the development of foaming and curing processes to obtain uniformity of physical properties within and between buns. Uniformity is important to achieve reproducible results during the characterization and selection of the various products.

The experimental work carried out and presented in this task includes the evaluation of microwave foaming techniques, curing methods, spray drying temperature and effect of these process parameters on the ILD values of the polyimide foams.

4.1.1 Foaming Techniques

A variety of foaming methods have been already evaluated during the course of NAS9-15050. These methods included dielectric, thermal, and microwave heating. Microwave heating proved to be superior in producing homogeneous cellular structure and was selected.

The development of the terpolymer powder precursor, 1720-1, the candidate foam precursor for the present program was carried out during the course of NAS9-15484. In the same contractual effort, extensive studies were carried out to develop optimum process parameters which were found to be adequate for foams produced in the 5 kW microwave oven. During the course of the same NAS9-15484 program, the scale-up of the foams derived from the 1720-1 precursors was initiated using the 15 kW GFE microwave oven (Ref. 3).

The foam samples produced in this oven were relatively free of visible flaws and imperfections and possessed a homogeneous cellular structure. Foam reticulation was recognized to be a critical imperfection and made it mandatory to carry out additional work. This imperfection proved to be the weakest part of the foam in fatigue testing and the principal cause of variability of physical properties within the bun. To overcome this deficiency, further optimization work was continued during the extension period of the NAS9-15484 program.

The work performed during this extension period involved studies of microwave power output and power pulsing. The ultimate objective of this work was to generate a parameter, kW/kg, relating microwave power (kW) to precursor weight (kg). To avoid reticulation, the optimum foaming conditions were found to be in the range of 0.6 to 1.0 kW/kg.

A timer device installed during the extension of the program permitted some preliminary evaluations of the effect of pulsing the microwave power ON and OFF during foaming. Due to time limitations, the only pulsing cycle tested was 60 seconds ON and 60 seconds OFF. Foams produced by this pulsing cycle and microwave power output at 0.84 kW/kg, although not completely free of reticulation, represented a considerable improvement in quality and were selected as the optimum candidate at the end of the contractual work carried out under NAS9-15484.

The data developed during the course of that program together with the process limitations reported above served as the starting point for this contractual effort, NAS9-16009.

The experimental work leading to foams with uniformity within and between buns was carried out in this current contract in accordance with the following sequence:

- Effect of microwave power output
- Effect of power pulsing
- Effect of precursor drying temperature

The foaming process used to develop the test data in this task was carried out by the free-rise technique only, using the 15 kW microwave oven (GFE).

All foams produced were characterized concurrently and in accordance with ASTM Designation D-3574-77 as specified in Section 3. Test data were derived for each of the following properties, indentation load deflection, compression set and density.

Effect of Microwave Power Output

This effort started with an evaluation of the ratio of the power output to powder loading (kW/kg) at a constant power pulsing. Foams were produced in

the 15 kW microwave oven using 10, 12.5, 15, 18, and 20 kg (22, 27.5, 33, 39.6, and 44 lbs) of powder precursors respectively at two different power levels. These power levels were 8.4 and 15.0 kW. This covered the range of power output to powder loading (kW/kg) ratios from 0.56 to 0.84. In all cases, homogeneous cellular structure was obtained with sporadic reticulated areas. These reticulated areas did not appear to have any geometrical relationship to the microwave cavity. The results of this study are summarized in Table 1. Results indicate that at the same microwave power output, the lower the power ratio (kW/kg), the higher the ILD values both at 25 and 65 percent deflection. Best results were obtained at a kW/kg ratio of 0.84 using a loading of 10 kg. At this ratio, the largest possible foam that could be produced in the 15 kW microwave oven was made using 18 kg (39.6 lbs) of powder precursor at a full power of 15 kW (kW/kg = 0.84). This foam is shown in Figure 20. The foam is free of flaws and almost completely free of reticulated areas.

The foaming experiments reported in Table 1 were carried out by free-rise microwave technique, followed by curing to achieve flexibility and resiliency. The curing processes investigated included thermal and microwave curing. No additives or fillers were used during this experimental study. Thermal curing was found to be effective only up to a powder loading of 5 kg (11 lbs). When larger powder precursor loading was used the foams did not cure due to poor heat transfer through the thermally insulating polyimide mass. Microwave curing was carried out by extending the foaming cycle for an additional 20-40 minutes followed by a short period of thermal heating to cure the outer uncured skin of the foam which is approximately 2.5 cm (1.0 in.) thick. This effort will be reported later in this same section.

Effect of Microwave Power Pulsing

This study was carried out by automatically switching the microwave power ON and OFF (one pulsing cycle) for a pre-determined length of time during the entire foaming and curing process. All foaming experiments were carried out at different pulsing cycles but at constant kW/kg ratio to determine the effect of power switching. The results of this study are summarized in Table 2.

Pulsing is a process which allows the heat generated in the foam to dissipate throughout the mass during the OFF cycle thus avoiding overheating. The heat dissipated does not produce additional foam rise since foam rise is observed only during the ON cycle. Based on these considerations, longer OFF time should theoretically produce lower foam rise and therefore higher foam density. This obviously is not always the case as shown by the data of Table 2.

Another important effect of pulsing was a visible reduction of the foam collapse usually experienced with the free-rise foaming techniques. Since the synergistic influence of foam rise and foam collapse is a twin phenomenon which occurs simultaneously during the foaming cycle, no attempt was made in this task to derive hard relationships between pulsing cycles and corresponding ILD values. This work was carried out in Task III where the adverse effects of foam collapse were eliminated by foaming in a mold.

Table 1

Effect of Microwave Power Output on Polyimide Foam Properties

RESIN	1720-1	1720-1	1720-1	1720-1	1720-1
Dryer Temp. °C Inlet	100	100	100	100	100
Outlet	67-70	67-70	67-70	67-70	67-70
Surfactant	AS-2	AS-2	AS-2	AS-2	AS-2
Concentration %	0.75	0.75	0.75	0.75	0.75
Sieve Size	#25	#25	#25	#25	#25
Powder Thickness, cms	11.4	11.4	11.4	11.4	11.4
in	4.5	4.5	4.5	4.5	4.5
Powder Loading, kg	10	12.5	15	18	20
lbs	22	27.5	33	39.6	44
Ratio, kW/kg	0.84	0.672	0.560	0.83	0.75
Preheat - Time (Min)	-	-	-	-	-
Power (kW)					
Foaming - Time (Min)	15	15	15	15	15
Power (KW)	8.4	8.4	8.4	15	15
Pulsing (ON/OFF)	60/20	60/20	60/20	60/20	60/20
Curing-Microwave					
Time (Min)	40	40	40	40	40
Power (kW)	10	10	10	10	10
Pulsing (ON/OFF)	60/20	60/20	60/20	60/20	60/20
Curing-Thermal					
Temp. (°F)	400-500	400-500	400-500	400-500	400-500
(°C)	204-260	204-260	204-260	204-260	204-260
Time (hrs)	1.5	1.5	1.5	1.5	1.5
Density (lbs/ft^3)	1.43	1.50	1.62	1.38	1.37
(kg/m^3)	22.9	24	25.9	22.1	21.9
Resiliency	55-60	55	55-60	60	60-65
ILD 25% lbf N	75 334	80 356	92 409	58 258	60 267
65% lbf N	288 1281	290 1290	410 1824	193 858	252 1121
Compression Set 90%	35.0	38.9	40.5	41.5	43.2
50%	10.4	15.9	7.9	14.4	14.1

The first three experiments reported in Table 2 were carried out at a constant ON time of 60 seconds. To minimize local overheating and prevent fast foaming rates which cause reticulated areas, pulsing cycles were tested with shorter ON time to offer a way to distribute and dissipate heat more evenly during the foaming process. When the ON time was reduced from 60 to 20 seconds, all traces of reticulation completely disappeared and the foams possessed a uniform cellular structure within the bun. Pulsing cycles with ON time

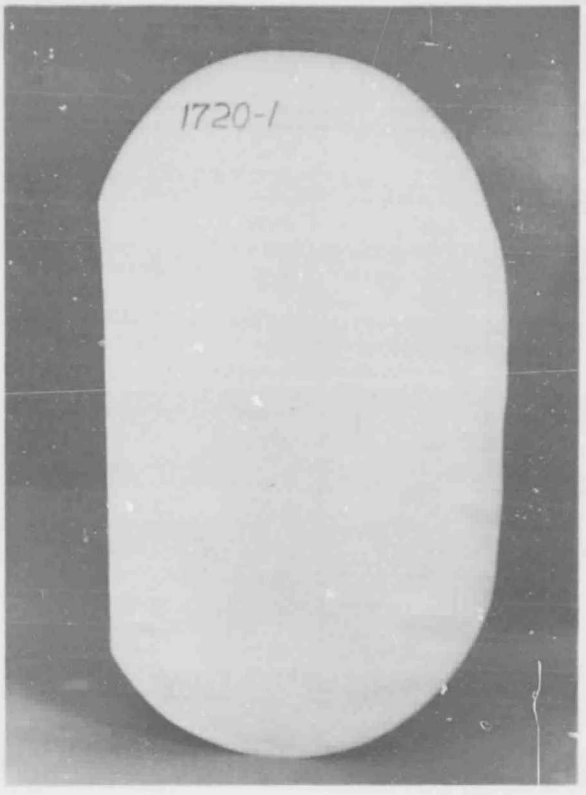


Figure 20.

Terpolyimide Foam: 15 kW Microwave Cavity at Full Power

shorter than 20 seconds were abandoned due to the excessively long foaming and curing time. The conditions selected in these initial studies were a pulsing cycle of 20 seconds ON and 20 seconds OFF at a kW/kg ratio of 0.84 using a powder loading of 10.0 kg (22 lbs). A foam produced at these conditions is shown in Figure 21. These pulsing conditions were used in all subsequent work carried out in Task I and Task II of this program and later selected as the optimum pulsing cycle time.

Effect of Precursor Drying Temperature

The major objective of this task was to develop foam uniformity within and between buns. To achieve this goal, it became necessary to produce and use powder precursors that were uniform in physical properties and volatile content. The quality standards set forth for powder precursors to assure uniform volatile content will be discussed in Task II and the optimization of the foam properties is presented below.

The degree of expansion of polyimide precursor during microwave foaming is dependent on the concentration of volatiles. The volatile content, a mixture of methanol and water that forms during the amidization and imidization reactions, depends on the outlet temperature of the drying process.

The process selected for converting the liquid resin to a powder precursor is based on a spray drying technique in which the outlet temperature is the

Table 2

Effect of Microwave Power Pulsing on Polyimide Foam Properties

RESIN	1720-1	1720-1	1720-1	1720-1	1720-1
Dryer Temp. °C Inlet	100	100	100	100	100
Outlet	67-70	67-70	67-70	67-70	67-70
Surfactant	AS-2	AS-2	AS-2	AS-2	AS-2
Concentration %	0.75	0.75	0.75	0.75	0.75
Sieve Size	#25	#25	#25	#25	#25
Powder Thickness, cms	11.4	11.4	11.4	11.4	11.4
in	4.5	4.5	4.5	4.5	4.5
Powder Loading, kg	10	10	10	10	10
lbs	22	22	22	22	22
Ratio, kW/kg	0.84	0.84	0.84	0.84	0.84
Preheat - Time (Min)	-	-	-	-	-
Power (kW)					
Foaming - Time (Min)	15	15	15	15	15
Power (KW)	8.4	8.4	8.4	8.4	8.4
Pulsing (ON/OFF)	60/20	60/40	60/60	20/20	10/10
Curing-Microwave					
Time (Min)	40	40	40	40	40
Power (kW)	10	10	10	10	10
Pulsing (ON/OFF)	60/20	60/40	60/60	20/20	10/10
Curing-Thermal					
Temp. (°F)	400-500	400-500	400-500	400-500	400-500
(°C)	204-260	204-260	204-260	204-260	204-260
Time (hrs)	1.5	1.5	1.5	1.5	1.5
Density (lbs/ft^3)	1.67	1.4	1.17	1.41	1.34
(kg/m^3)	26.7	22.4	18.7	22.6	21.4
Resiliency	55-60	55-60	70	65	60-65
ILD 25% lbf N	75 334	58 258	53 236	68 302	55 245
65% lbf N	288 1281	220 979	140 623	240 1068	207 921
Compression Set 90%	35.0	47.3	47.8	41.7	48.2
50%	10.4	14.4	10.5	12.3	8.5

most critical parameter. The study dealing with the effect of the outlet temperature of the spray dryer on precursor's properties was carried out by producing the powder precursors at four different temperature ranges of 67-70, 64-67, 60-64, and 56-60°C (152.6-158°F, 147.2-152.5°F, 140-147.2°F, and 132.8-140°F) respectively. The powder precursors were foamed in the 15 kW microwave oven at a kW/kg ratio of 0.84 using a powder loading of 10.0 kg (22 lbs) and a pulsing cycle of 20 seconds ON and 20 seconds OFF. The results of this study are summarized in Table 3.

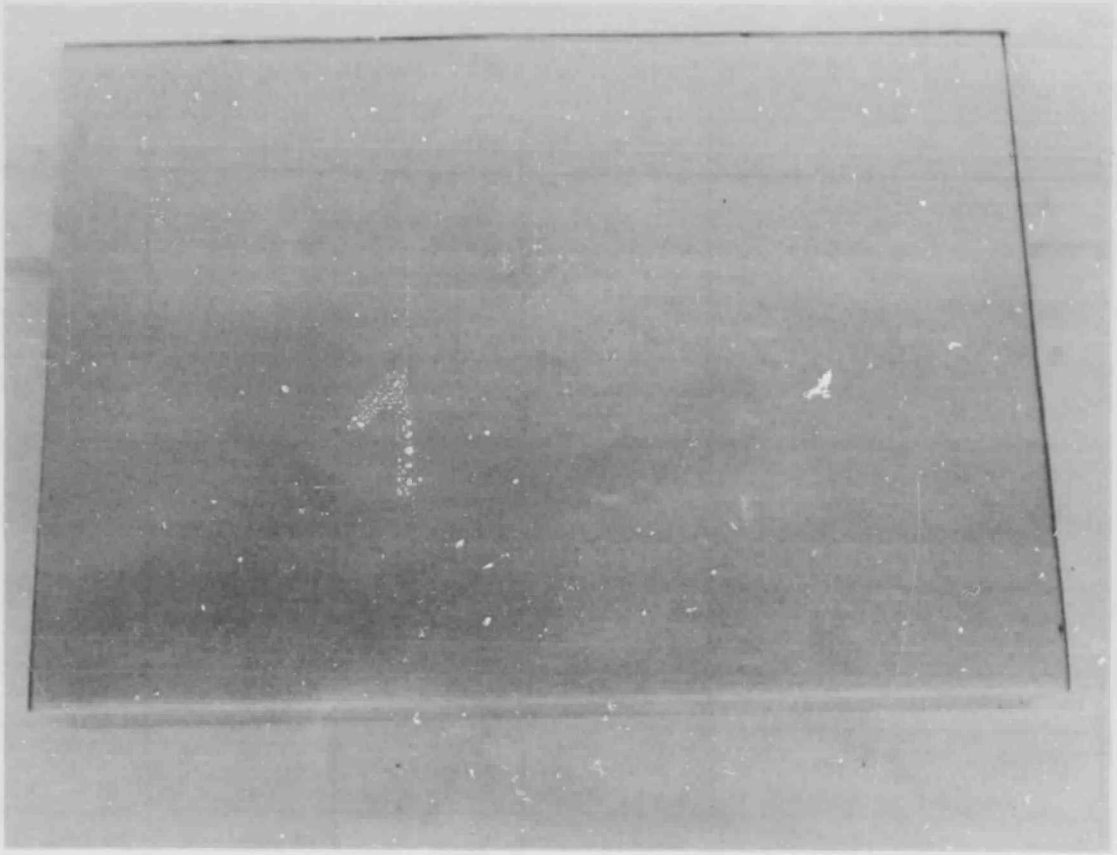


Figure 21. Polyimide Flexible, Resilient Foam Produced at 0.8 kW/kg and Pulsing Cycle of 20/20

The discussion of the effect of drying temperature on the mechanical properties of foams, with particular reference to indentation load deflection values is presented in Subtask 4.1.4 and the effect on cellular structure of the foams is discussed below.

The temperature of the spray dryer affects the foaming behavior of the precursors and dramatically alters the cellular homogeneity and structure of the foams. The homogeneity within bun and between buns improves as the outlet temperature decreases and reaches optimum conditions at the lowest temperature studied. At an outlet temperature of 56-60°C (132.8-140°F), the cellular homogeneity was significantly better than that obtained at higher temperatures. More significant is the fact that foam yield increased with a decrease of the outlet temperature reaching a maximum at 56-60°C (152.6-158°F). Temperatures lower than 56°C (132.8°F) produced wet powder which possessed short storage life due to caking. The foam produced at an outlet temperature of 56-60°C (132.8-140°C) is shown in Figure 22. During the study it was also found that the powder yield per hour increases proportionally as the temperature decreases. This relationship was later used as a quality control standard for the production of the powder precursors.

Table 3

Effect of Drying Temperature on Polyimide Foam Properties

RESIN	1720-1	1720-1	1720-1	1720-1
Dryer Temp. °C Inlet	100	100	100	100
Outlet	67-70	64-67	60-64	56-60
Surfactant	AS-2	AS-2	AS-2	AS-2
Concentration %	0.75	0.75	0.75	0.75
Volatile Content	20.7	21.4	21.7	22.3
Sieve Size	#25	#25	#25	#25
Powder Thickness, cms	11.4	11.4	11.4	11.4
in	4.5	4.5	4.5	4.5
Powder Loading, kg	10	10	10	10
lbs	22	22	22	22
Ratio, kW/kg	0.84	0.84	0.84	0.84
Preheat - Time (Min)	-	-	-	-
Power (kW)				
Foaming - Time (Min)	15	15	15	15
Power (KW)	8.4	8.4	8.4	8.4
Pulsing (ON/OFF)	20/20	20/20	20/20	20/20
Curing-Microwave				
Time (Min)	40	40	40	40
Power (kW)	10	10	10	10
Pulsing (ON/OFF)	20/20	20/20	20/20	20/20
Curing-Thermal				
Temp. (°F)	400-500	400-500	400-500	400-500
(°C)	204-260	204-260	204-260	204-260
Time (hrs)	1.5	1.5	1.5	1.5
Density (lbs/ft^3)	1.50	1.38	1.23	1.10
(kg/m^3)	24	22.1	19.7	17.6
Resiliency	65	60	65-70	70
ILD 25% lbf N	63 280	50 222	43 191	43 191
65% lbf N	217 965	159 707	136 605	154 685
Compression Set 90%	43.9	42.7	42.3	34.9
50%	12.9	11.1	9.2	8.7
Foam Yield, BF	65	82	90	95

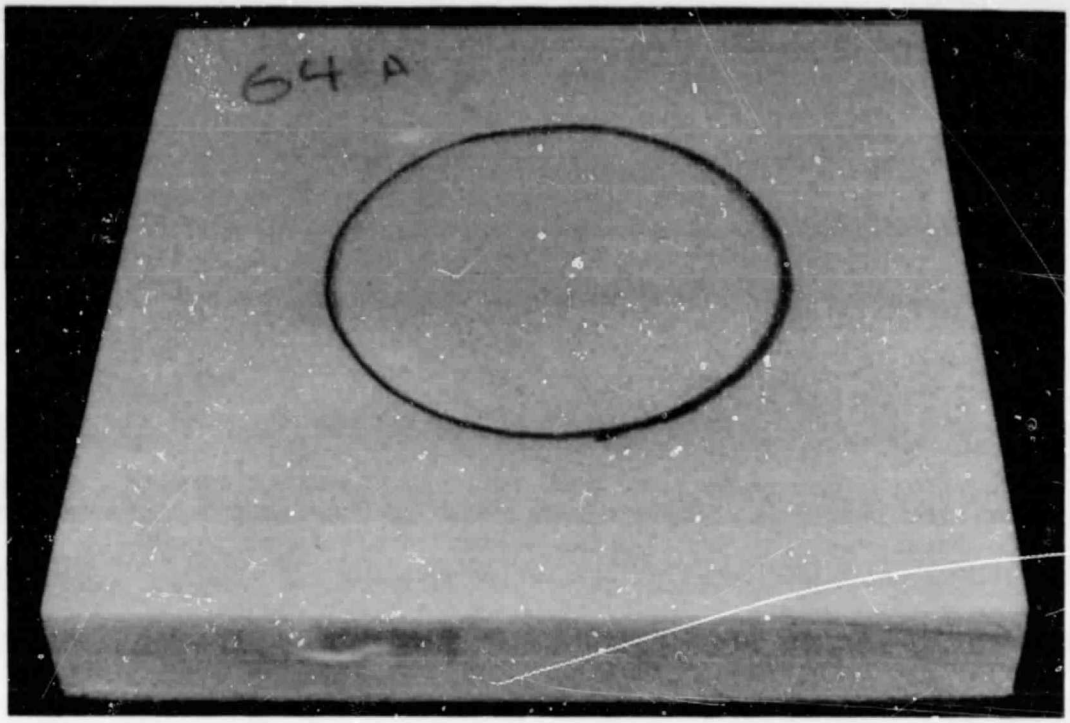


Figure 22. Terpolyimide Foam: Cellular Structure Produced at an Outlet Temperature of 56-60°C

The temperature that governs the homogeneity of the cellular structure of the foams was found to be exclusively the outlet temperature of the spray dryer. This parameter affects not only the cellular structure but the physical characteristics of the powder precursors and the mechanical properties of the foams. The influence of the outlet temperature on the characteristics of the powder precursors is discussed in Task III dealing with particle size distribution. The relationship of the outlet temperature and other processing parameters with foam properties is discussed in Section 4.1.4, where it was recognized that foams produced at low outlet temperatures possessed poor fatigue resistance and failed in less than 8,000 cycles.

4.1.2 Curing Techniques

In an electromagnetic field the polyimide powder precursors absorb energy at very high rate. This energy causes a temperature increase and foaming in a relatively short time (3-10 minutes). During this foaming step the precursors undergo an amidization reaction and form a cellular structure which is very friable because ring closure and polymerization has not occurred yet. The ring closure reaction requires a higher level of energy. During the ring closure complete imidization and polymerization occurs and a high molecular weight polyimide cellular structure is formed which is flexible and resilient.

The evaluation of suitable curing methods was essential to this program because uncured foams are fragile and large foams not easily transferred from one area to another for further processing. This evaluation was carried out in the following sequence:

- Curing by Thermal processes
- Curing by Microwave processes
- Curing by Microwave-Thermal processes

Curing by Thermal Processes

Thermal methods of curing have been used almost exclusively in the industry to fabricate polyimide compositions. The process simply involves heating the polyimide resin in an oven at a temperature in the range of 218-315°C (425-600°F) until complete imidization occurs.

The terpolyimide precursors evaluated in this subtask have been processed in a similar way using a cure cycle of 60-90 minutes at a temperature of 260°C (500°F). The process was found to be effective up to a powder loading of 5 kg (11 lbs). Larger loadings produced foam buns that were difficult to handle because of their fragility. A second more serious problem resulted from the fact that these large foams did not cure completely due to the poor heat transfer through the thermally insulating polyimide mass.

Thermal methods are still used to date to cure small foams (1 kg of precursor) but the process has been replaced by a more advanced method for large foams made in the 15 kW microwave oven. This process is based on microwave curing.

Curing by Microwave Processes

This curing method was accomplished by extending the foaming cycle in the microwave oven thus exposing the foamed mass to additional microwave energy. The interactions between the electromagnetic radiation and the uncured foams are too complex to be described here. A general model of the curing process is believed to be as follows. The foamed uncured mass is a complex polyamic resin possessing unreacted groups capable to interact with the microwave field. This interaction generates thermal energy which drives the reaction toward the imidization and complete polymerization. Once the polyimide is formed the material is completely transparent to the electromagnetic field and no more energy is absorbed. At this point the foam is completely cured.

Because the outer skin [2.5-5 cm (1-2 in.)] is subjected to high heat loss to the surrounding atmosphere, it remains completely uncured. Hence, a final thermal curing cycle was devised as described below.

Curing by Microwave-Thermal Processes

This effort started with evaluation of the effect of microwave power output on rate of curing. The rate of microwave curing was monitored by periodically inserting a microwave transparent probe into the foam which penetrated the uncured mass only. This method provided a technique to measure the depth of cured foam. The microwave curing cycle ended when the foam had cured to within a minimum of four inches from the outside edge. The curing process was carried out at a pulsing cycle of 20 seconds ON and 20 seconds OFF at various microwave power outputs which included 10, 11.7, 14, and 15 kW for a period of 30 minutes. The thermal curing in all cases was carried out at 204-260°C (400-500°F) for 1.5 hours. The foams produced during this effort were made by free-rise technique and possessed good homogeneous structure and were free of reticulated areas. One problem that has consistently plagued the reliable evaluation of physical properties of foams made by free-rise technique is the collapse and/or shrinkage of the foams during curing. This problem was eliminated in subsequent studies by foaming in open molds as reported in the next subtask.

The microwave-thermal method of curing terpolyimide precursors was selected as the best method to cure foams produced in the 15 kW microwave oven. The process was carried out by extending the foaming cycle by approximately 30 minutes at a power output of 10-15 kW, depending on powder loading, followed by thermal curing for 1.5 hours at 204-260°C (400-500°F) to cure the outer 2.5-5 cm (1-2 in.) layer of uncured foam. This process was optimized in a subsequent task dealing with molding techniques.

4.1.3 Foaming by Free and Constrained Rise

The foams used in these initial studies were produced exclusively by free-rise technique using the 15 kW GFE microwave oven. This method simply involves heating the powder precursor in the microwave oven permitting the foam to expand freely. The foam rise with this type of process was often erratic and the foams assumed irregular shapes. A second problem has been the reliable evaluation of the foams obtained by the free-rise process due to foam collapse. Foam collapse occurred exclusively with the 1720-1 terpolyimide precursors during the last part of the foaming proces continuing through the entire curing process. The density of the collapsed foams increased to values as high as 80 kg/m^3 (5 lbs/ft^3), affecting all density related properties, such as ILD.

To overcome this deficiency, various foaming techniques were evaluated. These techniques involved constraining the foam rise during the foaming and curing processes. The constrained rise technique was carried out by placing the powder into a shaped, microwave compatible mold and allowing the foam to conform to the shape of the mold. With this process, collapse was significantly reduced because the walls of the mold supported the cellular mass and minimized shrinkage and foam collapse. Initial mold foaming studies were carried out with open-ended cylindrical molds having a capacity of 113 liters (30 gallons) and 206 liters (55 gallons) respectively. The foams made in

these molds were of poor quality having an inner core consisting of a vertical series of flaws which propagated toward the periphery of the foam.

Using the cylindrical molds, fully constrained foaming was also evaluated employing a closed mold. This method produced complete mold filling, but the foam possessed excessive striations and large flaws due to the gas entrapped during foaming.

Despite these deficiencies, the experiments conducted proved the feasibility of foaming polyimide precursors in a mold and provided a method to overcome foam collapse experienced with the free-rise method. An open rectangular polypropylene mold was subsequently constructed because the cylindrical shape proved of limited value in this study. The open mold configuration was selected because it provided for the escape of the evolving gases, rather than trapping them in the foam as it was experienced with closed molds. This mold, having dimensions of 60 x 91.5 x 40.5 cm (24 x 36 x 16 in.) is shown in Figure 11, Section 3. The initial experiments with this mold were carried out in the 15 kW microwave oven at a kW/kg ratio of 1.0 using a powder loading of 5 kg (11 lbs) and a pulsing cycle of 20 seconds ON and 20 seconds OFF. Using these conditions, molding to a configuration was successfully accomplished.

The foams produced in this mold possessed a very homogeneous cellular structure and were free of flaws and reticulation for 40-50 percent of the total volume which is approximately equivalent to 15-20 percent usable foam. Foam collapse was negligible. Most of the flaws were found to occur in the bottom half of the foam and were characterized by larger cavities radiating in all directions from the center. The top 10 percent of the foam was also unusable due to flaws. These imperfections were obviously the result of large quantities of gaseous by-products which collected at the bottom of the mold and produced large cavities as they expanded through the foaming mass. To overcome this deficiency the mold was modified by installing a bottom grid and corner vents. This modification reduced the number of flaws in the bottom half of the foam but the usable foam yield did not increase.

A considerable amount of secondary thermal foaming was evident on the sides of the foams produced in the rectangular mold. This was believed to be the result of incomplete microwave foaming due to the cooling effect of the polypropylene mold. To reduce the heat losses, the sides of the mold were insulated with 2.5 cm (1 in.) thick polyimide foam liners which were fitted in place without the use of fastener or adhesives. This modification reduced the amount of secondary thermal foaming and increased the usable foam to about 25 percent.

With this study the basic process for microwave foaming polyimide precursors in a mold was established. The rectangular polypropylene open mold configuration modified with a bottom grid, corner vents and insulated with polyimide foam liners was selected for further optimization as will be reported in Task III.

4.1.4 Evaluation and Selection

The principal objective of this task is the identification and selection of processing conditions and fabrication methods which yield foams with uniformity in physical properties within and between buns. Foam uniformity is essential to arrive at a classification of the flexible resilient foams into five groups of products according to established ILD values.

The data and test results reported in this task were obtained from foams produced in the 15 kW microwave oven using free-rise techniques only, since at this early phase of the program other more advanced foaming processes were not yet developed.

The selection of the optimum parameters was carried out through a concurrent study of processing variables and fabrication methods in conjunction with characterization, testing and visual inspection. The results of this study was the identification of process parameters which not only produced foams with uniformity within and between buns, but also influenced the physical properties of these same foams to aid their classification into products. This was achieved by the identification of relationships between foam properties and processing parameters which included microwave power output, microwave pulsing methods and outlet temperature.

The data resulting from the studies of the effect of these three parameters are presented in Tables 1, 2 and 3 respectively. Graphical representations of these results are shown in Figure 23 for outlet temperature relationship, in Figure 24 for microwave power output relationship and Figure 25 for microwave pulsing relationship. The data reported in each of these graphs are briefly discussed below.

As shown in Figure 23 a direct relationship exists between outlet temperature and the values of density, ILD, and compression set. In the spray drying process, the outlet temperature controls the range of the volatile content of the precursors which in turn influences the foam rise and therefore foam density. Since higher force is required to deflect or compress foams of increasing densities, the direct relationship between ILD values and foam densities is theoretically expected. The effect of outlet temperature on the compression set values of the foams is less clearly understood, but may be related to improved elastic properties of the foams due to the more open cellular structure which is generally obtained from precursors with high volatile content. The lowest and most desirable values of ILD and compression set were obtained at an outlet temperature of 56-60°C (132.8-140°F). Foams derived from these precursors were foamed in the 15 kW microwave oven at a kW/kg ratio of 0.84 using a powder loading of 10 kg (22 lbs) and a pulsing cycle of 20 seconds ON and 20 seconds OFF.

Figure 24 shows the relationships between the power output expressed as kW/kg and the most critical foam properties. As apparent from the graph, an inverse relationship exists between the value of the kW/kg and those of the density, compression set, and ILD. This was expected since higher power output produces higher foam rise and correspondingly lower foam density and therefore

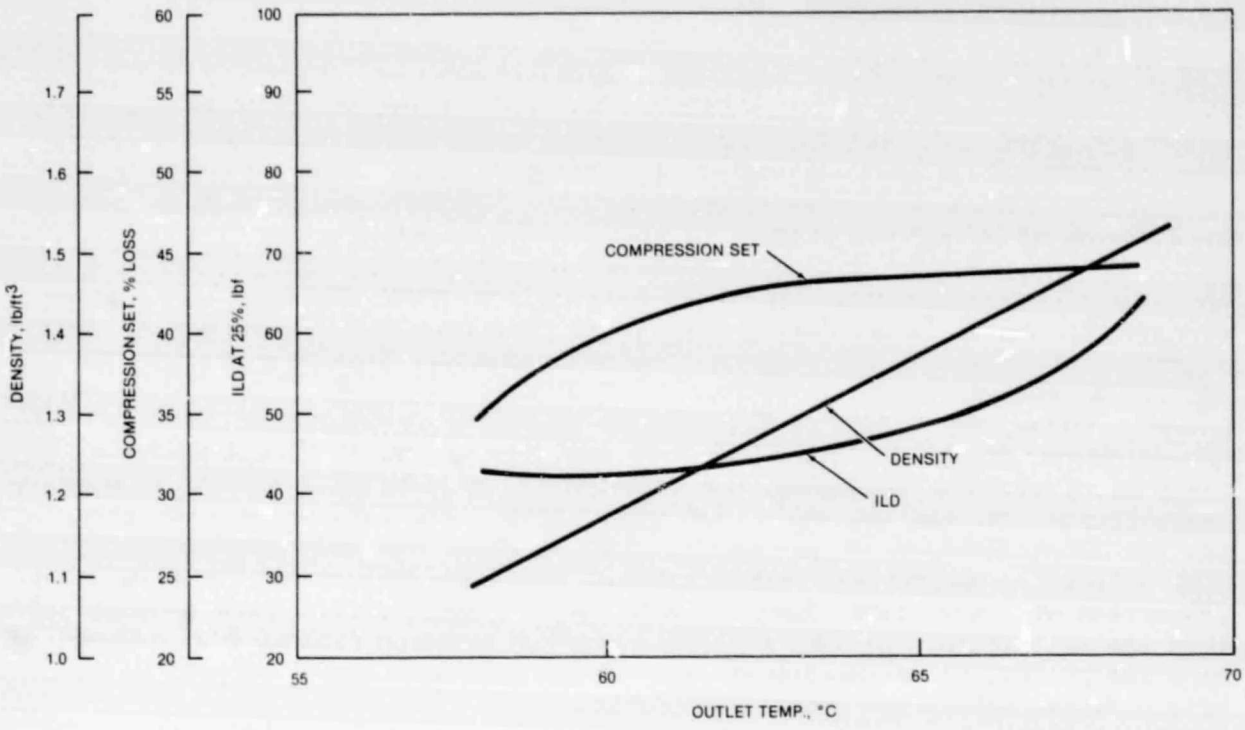


Figure 23. Effect of Outlet Temperature on Critical Properties of Polyimide Flexible, Resilient Foams

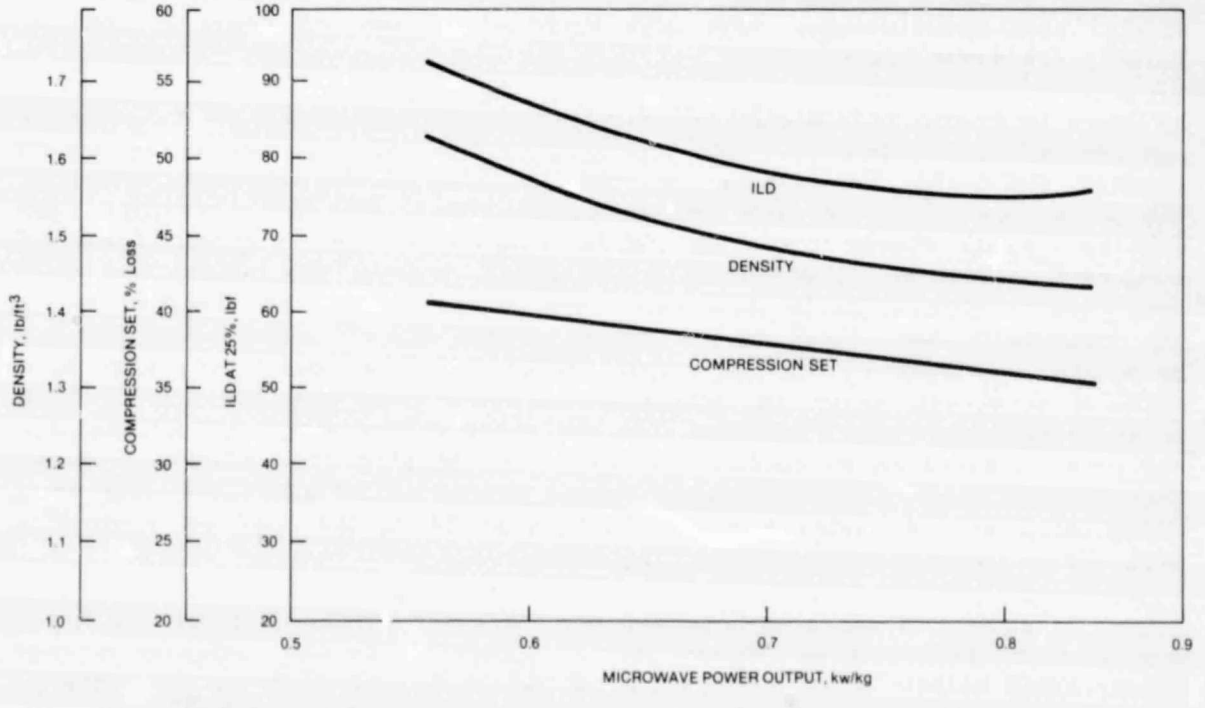


Figure 24. Effect of Microwave Power Output on Critical Properties of Polyimide Flexible, Resilient Foams

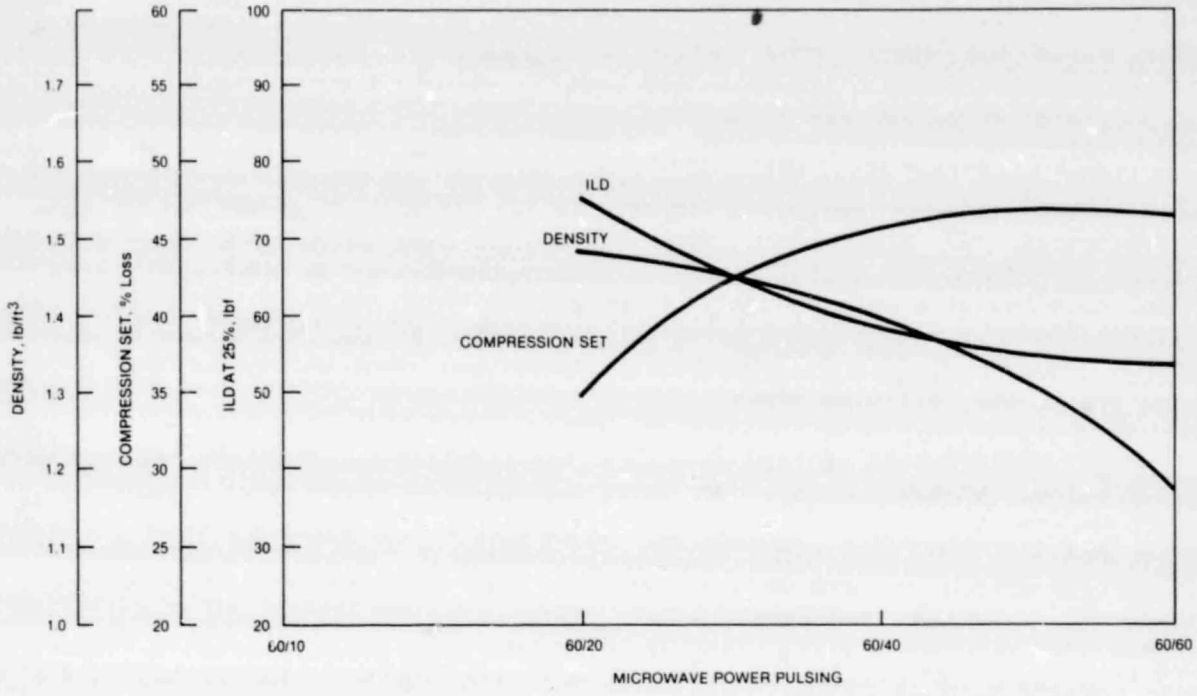


Figure 25. Effect of Microwave Pulsing on Critical Properties of Polyimide Flexible, Resilient Foams

lower ILD values. As in the case of the previous process parameter, the compression set value relationship is less understood.

As was previously discussed, the value of the power output plays a major role in controlling the uniformity of physical properties within and between buns. The optimum value to achieve uniformity was found to be 0.84 kW/kg using 10 kg (22 lbs) of powder precursor. This value was found to coincide with the point at which the ILD and compression set values of the foams are at the lowest levels, a characteristic that favors low density properties. The foams evaluated in this subtask were produced in the 15 kW microwave oven using a pulsing cycle of 60 seconds ON and 20 seconds OFF from powder precursors prepared at an outlet temperature of 67-70°C (152.6-158.0°F). This last process variable reflects the higher levels of the ILD and density reported in Figure 24.

The effect of pulsing the microwave power on these same critical properties is shown in Figure 25. These results are not immediately understood since longer OFF time during foaming is known to produce lower foam rise and consequently higher density and ILD values.

The mechanism of curing polyimide foams by the microwave method becomes more complex when pulsing is used because during the OFF cycle the condensation reaction stops. With this type of process, the microwave energy required to compensate for the heat dissipated during the OFF cycle increases as the OFF cycle is extended, resulting in less energy available for the condensation

reaction. Therefore, with long OFF cycle times the foams can never achieve a fully cured condition. This mechanism explains the lower ILD and density values and the higher compression set loss as the OFF time increases, typical of polyimide foams not fully cured.

Additional work was carried out by maintaining the ON and OFF times equal to each other. Pulsing cycles of 10/10, 20/20, 30/30, 40/40 and 60/60 were investigated. No significant contribution to foam properties were found except that long OFF cycles produced undercured foams, as discussed above. Foams produced at a pulsing cycle of 20/20 and 30/30, however, were found to possess the most homogeneous cellular structure. At the conclusion of this work a pulsing cycle of 20/20 was selected and used throughout the work reported in the following tasks.

The major contribution of this study was the elimination of reticulated areas which helped produce foams with more homogeneous properties within bun.

In accordance with the major objective of Task I, uniformity of physical properties within bun and between buns has been attained and optimum processes and parameters selected. Foams produced in the 15 kW microwave oven from powder precursors spray dried at an outlet temperature of 56-60°C (132.8-140°F) using a kW/kg ratio of 0.84, a powder loading of 10 kg (22 lbs) and a pulsing cycle of 20 seconds ON and 20 seconds OFF followed by microwave curing at 14 kW and a final thermal curing at 232-246°C (450-475°F), possessed the most homogeneous cellular structure with uniformity in physical properties within and between buns, without flaws, imperfections or reticulated areas. With these studies, the effort of Task I was completed, but the evaluation of certain parameters, such as outlet temperature, was more succintly studied in subsequent tasks to establish foam classification.

TASK I - Foam Fabrication Studies - Summary

The following brief review describes the major developments resulting from the experimental work carried out in Task I, Foam Fabrication Studies.

1. Foams produced in the 15 kW (GFE) microwave oven from powder precursor dried at an outlet temperature of 56-60°C (132.8-140°F) using a microwave power ratio of 0.84 kW/kg at a loading of 10.0 kg (22 lbs) and a pulsing cycle of 20 seconds ON and 20 seconds OFF followed by microwave curing at 14 kW and thermal curing at 232-246°C (450-475°F), have consistently shown to possess uniformity in physical properties within and between buns, without flaws, imperfections or reticulated areas.

2. A direct relationship was found to exist between outlet temperature and the values of density, ILD, and compression set. The lowest and most desirable values of ILD and compression set were obtained at an outlet temperature of 56-60°C (132.8-140°F).

3. The cursory experiments conducted proved the feasibility of foaming polyimide precursors in a mold and provided a method to overcome

foam collapse, a major deficiency of free-rise technique. A basic process for foaming polyimide precursors in a mold was established. The rectangular polypropylene open mold configuration modified with a bottom grid, corner vents, and insulated with polyimide foam liners was selected for further optimization in Task III.

4.2 TASK II - FORMULATION AND OPTIMIZATION

The primary objective of this task is to develop precursor formulations and process parameters to achieve foams with multiple density characteristics and specific ILD values for use in seating applications.

The second objective is to establish quality control measures to aid in the consistent production of polyimide foams to attain the desired levels of comfort.

The effort of this task will be pursued through seven separate but complementary schemes. A discussion of the experimental studies carried out is described below.

4.2.1 Blowing Agents

This task involves modification of the mechanism of foam formation by the incorporation of blowing agents to produce polyimide foams with a larger cellular structure and a wide range of comfort/hardness characteristics.

Blowing agents have been used to produce both rigid and flexible conventional plastic foams in commercial scale. They are either solid, liquid or gaseous substances and regardless of their physical state they function by evolution of a gas at well defined decomposition temperatures. A liquid blowing agent is already present in the polyimide precursor and is generated in situ within the matrix of the polymer. This blowing agent is a mixture of water and methanol which forms during the polymerization reaction as illustrated in the sequence of reactions shown in Section 3. Gaseous blowing agents, such as nitrogen, were not adaptable to polyimide foam processing since holding the nitrogen under pressure in the polymer melt requires the use of specialized equipment. Only solid blowing agents were evaluated in this task.

Solid blowing agents are organic or inorganic materials that decompose under the influence of heat to yield a gaseous component. The decomposition temperature determines the usefulness of a foaming agent and governs the conditions under which this component is to be processed.

The blowing agents tested in preliminary evaluations included Celogen TSH, Celogen OT, Celogen A 2130, Celogen RA, Celogen HT 550, Nitropore ATA, Nitropore OBSH, Kempore 125, Expandex 5 PT, Tinuvin 320, Tinuvin P, ammonium bicarbonate, sodium bicarbonate, sodium borate, boric acid, triphenyl phos-

phate, disodium phosphate, dimethyl phthalate, phthalic acid, benzoic acid, ammonium benzoate, and benzene sulfonyl hydrazide.

Screening of the optimum blowing agent was carried out by compounding the blowing agent in the powder precursor at a concentration of 1 percent based on polyimide solids followed by microwave foaming in the 5 kW Model 4115 cavity. The foams were subsequently cured in the thermal oven at a temperature of 121-248°C (250-480°F). All foams were made from 1720-1 precursors modified with 0.75 percent AS-2 and inspected visually to screen out the most likely candidates.

A large number of these additives interfered with the foaming mechanism preventing foam rise, while others produced foams of various density and flexibility. The most promising candidates are reported in Table 4.

Of all the blowing agents studied in this effort, Celogen HT 550, Expandex 5 PT and sodium bicarbonate produced flexibility as well as larger cellular structure.

The foams made with Celogen HT 550 appeared to be better in quality and possessed considerably lower density than those made with the other two candidates. The larger cellular structure obtained with this blowing agent is illustrated in Figure 26. The foams shown were prepared from the same precursor but the bottom foam was modified by the addition of the blowing agent. The larger cellular structure obtained with the use of the blowing agent is shown magnified in Figures 27 and 28.

Table 4

Evaluation of Blowing Agents

BLOWING AGENT	DECOMPOSITION TEMP.		FOAM CHARACTERISTICS	DENSITY	
	°F	°C		lbs/ft^3	kg/m^3
Celogen TSH	220-270	104-132	Brittle cellular structure	1.7	27.2
Celogen OT	300-350	149-176	Brittle cellular structure	1.5	24.0
Triphenyl Phosphate	120-124	49-51	Rigid foam	8.6	137.6
Celogen RA	420-500	215-260	Rigid foam	9.1	145.6
Celogen HT 550	550-600	287-315	Flexible, resilient foam homogeneous cellular structure	0.9	14.4
Nitropore ATA	250-400	121-204	Brittle cellular structure	-	-
Benzene Sulfonyl Hydrazide	212	100	Rigid foam	5.9	94.4
Ammonium Benzoate	388	198	Rigid foam	6.1	97.6
Expandex 5 PT	464-482	240-250	Semi flexible foam homogeneous cellular structure	3.1	49.6
Sodium Bicarbonate	518	270	Flexible, resilient foam homogeneous cellular structure	1.0	16.0

Figure 26. Terpolyimide Foams Produced With (Foam 195) and Without Blowing Agent (Foam 98)

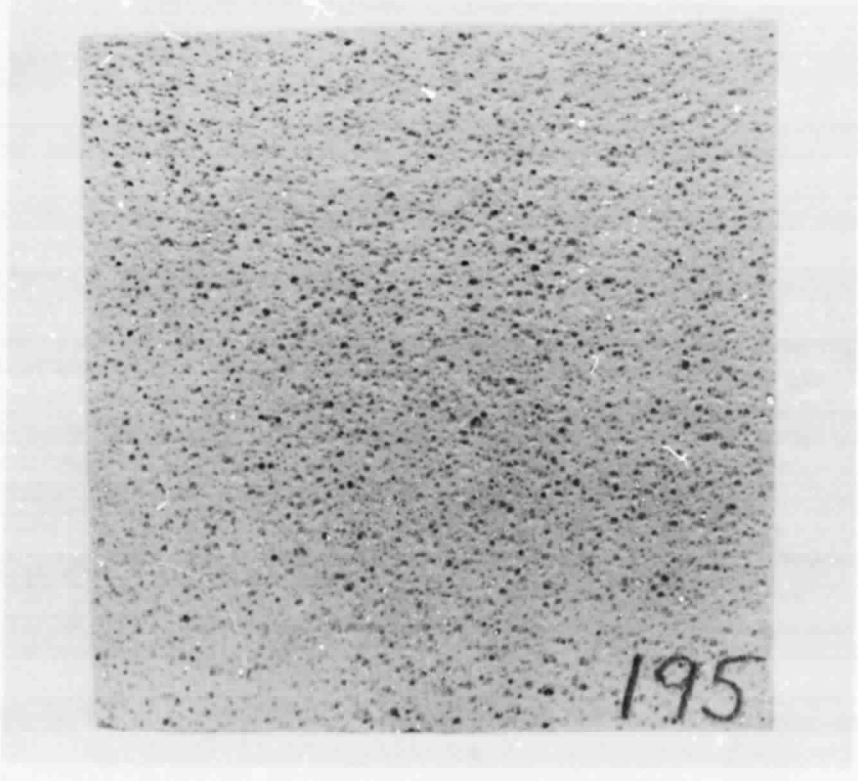


Figure 27. Cellular Structure of Terpolyimide Foams Produced With Blowing Agent

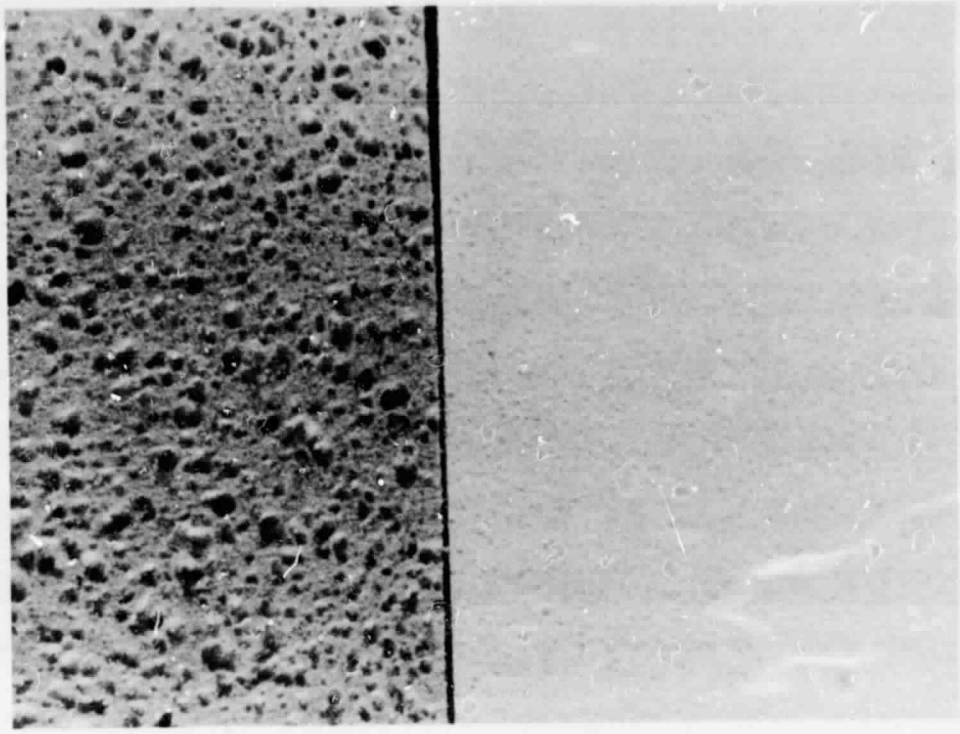


Figure 28. Cellular Structure of Terpolyimide Foams Produced With (Left) and Without (Right) Blowing Agent

Celogen HT 550 was selected as the optimum candidate for studies dealing with the effects of blowing agent concentration on density and ILD values of the foams. Celogen HT 550 was added in powder form and rolled in a jar mill with the powder precursor for 1 hour for uniform distribution. All foams were made in the 5 kW microwave oven using a power output of 2.5 kW at a loading of 1.0 kg and subsequently cured in a thermal oven at 121-248°C (250-480°F) for a period of 1.5 hours. Concentrations of Celogen HT 550 of 0, 0.25, 0.5, 1.0, 2.5, and 5.0% respectively were used and the foams evaluated for ILD and compression set values. Results of this study are presented in Table 5 with the foams produced shown in Figure 29 where the effect of increasing concentration of the blowing agent on the cellular structure from bottom (0%) to top (5.0%) is evident. As shown in this figure, the cellular structure becomes more open with increasing concentrations of blowing agent. The density of these foams should decrease with increasing concentration of the blowing agent, but as shown in Table 5, the correlation is rather poor. This is attributed to the deficiency of free-rise foaming techniques whereby foams undergo collapse during the curing cycle and produce variability within the bun thus preventing accurate determination of properties.

A series of experiments were subsequently carried out in the 15 kW GFE microwave oven to study the effect of particle size of the blowing agent on foam properties. These experiments were performed at three different power ratios of 1.0, 1.3 and 1.7 kW/kg respectively using a constant powder loading of 8.235 kg (18 lbs) and a blowing agent concentration of 2.5 percent. The results of this study are reported in Table 6.

Table 5

Celogen HT 550 - Effect of Concentration on
Properties of Terpolyimide Foams

FOAM NO.	CONC. OF BLOWING AGENT %	DENSITY		COMPRESSION SET		ILD			
		lbs/ft^3	kg/m^3	90%	50%	25%		65%	
						lbf	N	lbf	N
24	0	0.88	14.0	34.4	11.5	20.7	92.0	84.[illegible]	374.5
21	0.25	0.65	10.4	32.5	12.2	19.8	88.0	78.4	348.7
20	0.5	0.96	15.3	36.8	11.7	38.6	171.6	118.0	524.8
22	1.0	0.66	10.5	25.7	10.1	20.5	91.1	71.1	316.2
25	2.5	0.88	14.0	34.4	11.5	20.7	92.0	84.2	374.5
19	5.0	0.59	9.4	28.9	10.4	15.0	66.7	57.0	253.5

Figure 29.
Celogen HT 550 Blowing Agent - Effect of Concentration on Cellular Structure

The data show that the particle size of the blowing agent does not have discernable effect on the compression set and ILD values of the foams produced at the three power levels reported above, although the cell size of the foams decreased with the particle size of the blowing agent. The foams produced at different particle sizes are shown in Figure 30. The property which was found to be very dependent on the blowing agent particle size was the dynamic fatigue as shown in Figure 31, where the data points were obtained by averaging results at all power levels.

Table 6

Summary of Particle Size Effect of Celogen HT 550 on Foam Properties

	1.3 kW/kg 10.7 kW 8.235 kg					1.7 kW/kg 14.0 kW 8.235 kg					1.0 kW/kg 8.2 kW 8.235 kg				
BM Hrs.	0	2	4	6	8	0	2	4	6	8	0	2	4	6	8
Foam #	58	54	55	56	57	21	64	61	62	63	104	65	66	67	68
Rough Cut, in.	31x36x12.5	33x38x915	31x37x13	32x38x13	32x38x14	32x38x14	38x32x14.5	38x30x11	38x32x13	30x36x14	32x38x13	37x32x14.5	35x32x14	32x38x13.5	32x38x13.5
Wt,lbs.	6.5	6.5	6.0	6.0	6.0		8.0	4.0	7.0	6.5	6.0	6.5	6.0	5.5	6.5
Yield, %	44.8	44.8	41.4	41.4	41.4	57.8	55.2	27.3	48.3	44.8	41.4	44.8	41.4	37.9	44.8
Density, lbs/ft^3	0.69	0.68	0.63	0.66	0.60	0.65	0.75	0.98	0.73	0.68	0.72	0.71	0.70	0.68	0.66
Compression Set															
90%	37.0	25.4	45.9	28.2	30.5	37.3	36.4	20.1	33.1	33.3	34.9	45.4	40.0	48.8	53.0
50%	12.8	11.5	13.6	9.8	11.9	11.8	14.0	8.6	11.2	8.9	12.9	16.2	13.4	15.6	16.3
ILD, lbf 25%	30.4	27.8	34.7	35.4	31.7	26.2	35.4	36.3	37.5	32.9	32.2	30.1	27.4	32.7	32.7
65%	96.4	86.0	108.8	114.3	106.7	114	106.3	120	113.9	109.7	122	107.9	87.2	119.1	124.9
Fatique															
% Thickness Loss	21%	31.8	7.7	17.1	17.5	4.1	16.5	1.3	2.6	5.3	53%	19.4	27.5	34.1	32.5

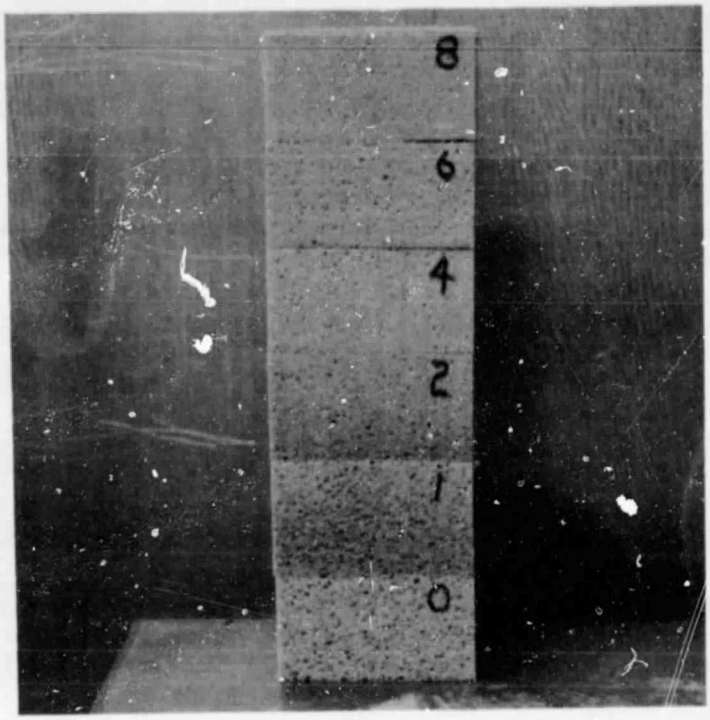


Figure 30. Effect of Particle Size of the Blowing Agent on Cellular Structure of Polyimide Foams at Various Ball Mill Hours

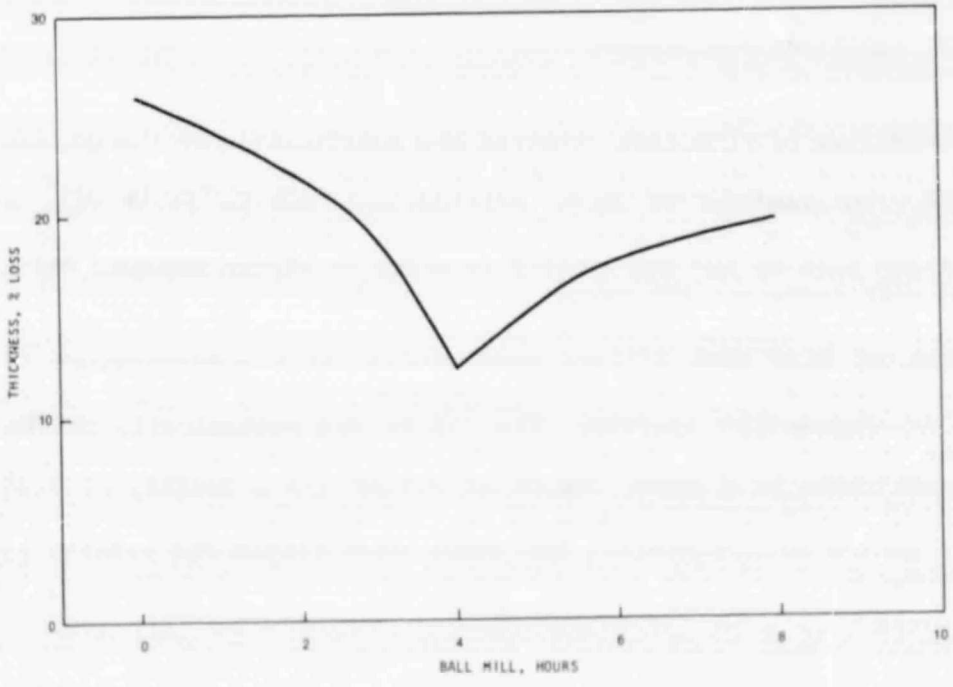


Figure 31. Effect of Ball Mill Hours on Dynamic Fatigue - % Loss in Thickness (Average of all Power Levels)

A second blowing agent parameter studied was the concentration of the blowing agent and its effect on foam properties. This effort was carried out by preparing powder precursor compositions at 0, 0.25, 0.5, 1.0, 2.5, 5.0 and 7.5 percent blowing agent. These compositions were foamed in the 15 kW microwave oven at a power ratio of 1.0, 1.3 and 1.7 kW/kg respectively, using a constant powder loading of 8.235 kg (18 lbs). A particle size for the blowing agent of 100-180 micron was selected for the study. The foams were characterized for the most critical properties and results reported in Table 7.

The density and the ILD values of the foams decrease with increasing concentrations of the blowing agent. This is evident for power levels of 1.0 and 1.3 kW/kg respectively but as the power ratio is increased to 1.7 kW/kg the scatter of result is excessive. This is attributed to the collapse of the foams caused by the excessive heat generated within the bun at high power levels.

The effect of the blowing agent concentration on the ILD values of the foams is shown in Figure 32 where the data points were obtained by averaging the values for all three power levels.

The major contributions of this initial study were the identification of parameters which provided methods to vary the ILD and density of the foams and the effect of power ratio on uniformity of cellular structure and variability of foam properties. Based on these results, Celogen HT 550 was selected as the candidate blowing agent for scale-up in the 15 kW microwave oven. This scale-up was successfully carried out in Task III employing the process parameters developed during the preliminary evaluation of foam fabrication studies discussed in this task and in Task III.

4.2.2 Additives and Fillers

The objective of this task involved the modification of the polymer structure with colloidal dispersions of substances such as silica, barium sulfate and others. The purpose of such modifications was to study the influence of these fillers on the important mechanical and physical characteristics of the foams such as ILD and density in order to afford new methods of obtaining foams with different ILD values.

A total of five such fillers were studied at a concentration of 5 percent based on polyimide solids. These included silica, calcium carbonate, clay, alumina, and barium sulfate. The filler was mechanically blended with the powder precursor in a jar mill. The compositions were then foamed in 5 kW microwave oven at a power output of 2.5 kW and a loading of 1.0 kg. These foams were subsequently cured in a thermal oven at 121-248°C (250-480°F) for a period of 1.5 hours. All foams were tested and results presented in Table 8.

Table 7

Summary of Celogen HT 550 Concentration Study

	1.0 kW/kg 8.2 kW 8.235 kg BM 4 hours							1.3 kW/kg 10.7 kW 8.235 kg BM 6 hours							1.7 kW/kg 14.0 kW 8.235 kg BM 4 hours						
Concentration of Blowing Agent, %	0	0.25	0.5	1.0	2.5	5.0	7.5	0	0.25	0.5	1.0	2.5	5.0	7.5	0	0.25	0.5	1.0	2.5	5.0	7.5
Foam #	83	98	84	85	86	87	101	78	99	79	80	81	82	103	73	100	74	95	76	77	102
Rough Cut In.	10x36x11	31x36x13.5	32x35x10.5	31x37x12	32x38x13	34x39x15.5	30x35x12	29x38x10	31x38x12.5	30x38x11.5	30x38x10.5	32x39x16	32.16x13	31.5x38x12	29x37x11.5	30x38x10	28x36x7	30x37x9.5	31x32x12.5	30x37x8	36x38x9
Lbs.	6.0	7.0	6.0	6.5	6.0	6.5	5	6.75	6.5	6.5	6.25	7.0	6.5	5.0	7.0	6.0	6.5	5.75	6.5	4.0	4.0
Yield %	41.4		41.4	44.8	41.4	44.8		46.6		44.8	43.1	48.3	44.8		48.3	44.8	39.7	44.8	27.6		
Density lbs/ft^3	0.98	0.96	0.87	0.87	0.81	0.60	0.60	1.20	0.94	1.13	0.93	0.63	0.54	0.60	0.82	0.94	0.82	1.11	0.78	0.93	0.96
Compression Set 90	30.6	40.9	28.7	24.8	20.4	26.2	26.0	31.3	16.9	19.3	20.2	31.7	20.0	18.2	40.1	17.9	2.13	20.6	20.1	20.8	14.9
50	9.0	12.5	8.0	7.4	8.2	10.0	10.7	11.0	7.1	7.9	8.6	11.5	8.1	8.3	9.0	7.3	8.3	9.9	8.6	8.7	8.0
ILD, lbf 25%	58	51.6	51	50	48.1	34	27.1	65.5	45.3	61	62	35.5	35	20.8	45.0	31.5	55.7	25.3	36.3	41.2	40.6
65%	247	197	211	190	160.1	109	74	338	140	222	240	119	154.5	53.9	175	111	197	114	120	148	115
Fatigue Loss Thickness %	2.4	11.5	4.1	3.05	4.19	18.7	53.9	15.3	13.9	4.65	1.6	33.8	2.6	23.5	1.4	18.0	0	0.8	17.5	3.7	6.3

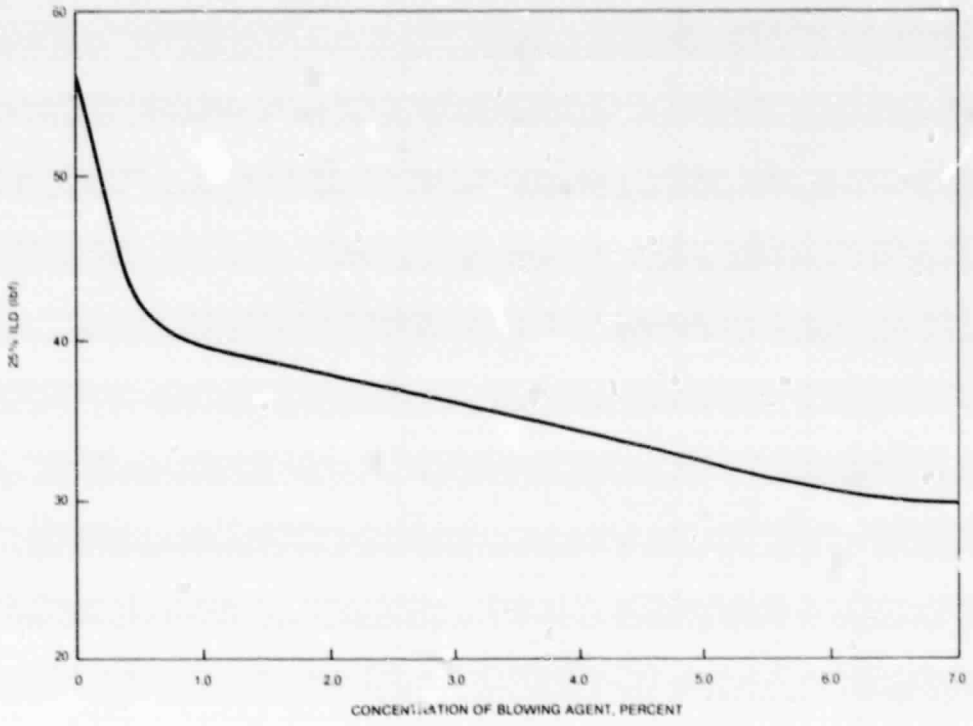


Figure 32. Effect of Blowing Agent Concentration on ILD Values of Polyimide Foams

Results of this study indicate that the incorporation of fillers into polyimide precursors do not produce foams with a wide spectrum of densities or ILD characteristics as expected. This task was continued with evaluation of conductive fillers in accordance with the plan.

The interaction of conductive fillers such as carbon, graphite, and aluminum powders with microwave energy was reported (Ref. 3) previously. The data reported showed that these conductive fillers added to polyimide powder precursors produce sufficient thermal energy in a microwave field to cause foaming and curing at relatively low power outputs. This technique was re-evaluated in this task in an attempt to achieve various levels of density and ILD characteristics at different concentrations of the conductive fillers.

The conductive filler evaluated was activated carbon which had previously shown (Ref. 3) to yield the best quality foam in a one-step microwave foaming-curing process. In the studies carried out during the execution of the present program it was established that variation of the concentration of the conductive filler produces a variation of the rate of curing without detectable effect on the properties of the foams. Since the properties of importance to the objective of the program were not affected, namely, density and ILD values, the work on this task was terminated at this point.

Table 8

Effect of Fillers on Properties of Terpolyimide Foams

Filler/Additive	Density		Compression Set		ILD				Foam Characteristics
					25%		65%		
	lbs/ft^3	kg/m^3	90%	50%	lbf	N	lbf	N	
None	0.89	14.2	37.8	10.4	18.2	80.9	64.4	286.4	Flexible, resilient, homogeneous cellular structure
Silica	0.96	15.3	38.5	10.4	21.2	94.2	80.1	356.2	Flexible, resilient, homogeneous cellular structure
Calcium Carbonate	1.04	16.6	33.2	11.0	24.4	108.5	85.8	381.6	Flexible, resilient, homogeneous cellular structure
Clay	0.82	13.1	40.3	11.2	21.3	94.5	76.8	341.6	Flexible, resilient, homogeneous cellular structure
Alumina	0.97	15.5	36.2	10.7	20.4	90.7	78.1	347.3	Flexible, resilient, homogeneous cellular structure
Barium Sulfate	0.61	9.8	51.9	22.5	25.8	114.8	86.0	382.5	Flexible, resilient, homogeneous cellular structure

4.2.3 Re-Evaluation of AS-2 Surfactant

The objective of this task was the re-evaluation of the best surface active agent developed under NAS9-15484. This re-evaluation was directed to establish relationships, if any, between surfactant concentration and foam properties such as density, ILD, and comfort index.

The first exploratory experiments were carried out in the 5 kW microwave oven with powder precursors modified with only 0.1, 0.25, 0.5, 0.75, 1.0, and 1.5 percent AS-2, respectively. All foams were made at a power output of 2.5 kW and a loading of 1.0 kg by free rise techniques. These foams were subsequently cured at 121-248.8°C (250-480°F) in a thermal oven for a period of 1.5 hours. The foams were tested and fully characterized for properties such as density, compression set, and ILD values. The results of this study are presented in Table 9. The compression set and ILD properties of the foams appear to be little affected by a change of the surfactant concentration. The significance of these data is expressed by the value of the comfort index which is defined as the ratio of the ILD value at 65 percent deflection to that at 25 percent deflection. The comfort indexes reported are in the range of 3 to 4 and fall within the acceptable range for seating comfort. This ratio is an empirical value only and does not take into account foam quality. As shown in Table 9, the foams produced at an AS-2 concentration below 0.25% possess a brittle cellular structure and are unsuitable for seat cushion applications in spite of their low comfort index value.

The studies concerning the re-evaluation of the surfactant concentration were continued in large scale using the 15 kW microwave oven. These studies

Table 9

Effect of AS-2 Surfactant Concentration on Properties of Terpolyimide Foams Produced in the 5 kW Microwave Oven

AS-2 CONC. %	DENSITY		COMPRESSION SET		ILD				COMFORT INDEX	FOAM CHARACTERISTICS
					25%		65%			
	lbs/ft^3	kg/m^3	90%	50%	lbf	N	lbf	N		
0.1	1.05	16.8	32.0	11.3	48.1	215.2	187.0	831.7	3.89	Slightly brittle and non-homogeneous structure
0.25	0.73	11.7	29.3	10.8	31.7	141.0	106.0	471.4	3.34	Flexible, resilient, homogeneous cell structure with some flaws
0.50	0.68	10.8	29.0	12.6	25.3	112.5	103.0	458.1	4.07	Flexible, resilient, homogeneous structure
0.75	0.73	11.7	26.8	10.0	28.5	126.7	102.0	453.6	3.58	Flexible, resilient, homogeneous structure. Minimal collapse.
1.0	0.86	13.7	39.4	10.3	40.5	180.1	149.0	662.7	3.68	Flexible, resilient, homogeneous structure. Good foam. Good tactile comfort. Some collapse.
1.5	0.85	13.6	29.4	9.5	22.8	101.4	116.4	517.7	5.1	Flexible, resilient, homogeneous structure

were carried out with powder precursors spra· dried at an outlet temperature of 56-60°C (132.8-140°F), modified only with 0.15, 0.25, 0.375, 0.5, 0.75, 1.0, and 1.5 percent AS-2 respectively. Foaming was carried out by free-rise technique using a kW/kg ratio of 0.84 at a loading of 10.0 kg and a microwave pulsing cycle of 20 seconds ON and 20 seconds OFF. These foams were microwave cured at a power output of 10.0 kW for a period of 40-45 minutes prior to thermal curing at 204-260°C (400-500°F) for a period of 1.5 hours. The results of this study are presented in Table 10. The foam properties reported in this table do not exhibit the same dependence on surfactant concentration as the foams produced in the 5 kW microwave oven, shown previously in Table 9. This discrepancy is attributed to a higher level of foam collapse occuring in the larger bun size produced in the 15 kW microwave cavity. This collapse accounts for the higher foam densities and for the correspondingly higher ILD values than those obtained in the 5 kW microwave cavity at the same surfactant concentration. The change of the critical properties of foams produced in the 15 kW microwave cavity illustrates the influence of scale-up on the foaming process. This problem has been fully evaluated in Task III dealing with optimization of the foaming parameters and in Task IV where the process for the five classes of foams was defined.

The foams produced at an AS-2 concentration of between 0.5 to 1.0 percent met the fatigue requirements and possessed the best comfort index with homogeneous cellular structure. At AS-2 concentrations lower than 0.5 percent, foam brittleness and non-homogeneous cellular distribution with large number of flaws were observed, as expected.

Table 10

Effect of AS-2 Concentration on Properties of Terpolyimide Foams Produced in the 15 kW Microwave Oven

FOAM NO.	AS-2 CONC. %	DENSITY		COMPRESSION SET		ILD				COMFORT INDEX	FOAM CHARACTERISTICS
						25%		65%			
		lbs/ft^3	kg/m^3	90%	50%	lbf	N	lbf	N		
87	0.15	1.31	20.9	33.6	9.7	70.0	311.3	220.0	978.5	3.14	Brittle cellular structure with some flaws
86	0.25	0.98	15.6	36.1	8.4	39.3	174.8	125.0	-556.0	3.18	Flexible, resilient, non-homogeneous cellular structure
102	0.375	0.96	15.3	36.8	10.6	42.3	188.1	139.0	618.2	3.29	Flexible, resilient, homogeneous cellular structure with some flaws
84	0.5	1.09	17.4	49.5	9.4	43.2	192.1	162.0	720.5	3.75	Flexible, resilient, homogeneous cellular structure
64	0.75	1.04	16.6	35.5	9.9	52.7	234.4	184.0	818.4	3.49	Flexible, resilient, homogeneous cellular structure
77	1.0	1.03	16.4	31.6	9.2	45.5	202.3	154.0	684.9	3.38	Flexible, resilient, homogeneous cellular structure
83	1.5	0.88	14.0	45.1	11.8	38.0	169.0	129.0	573.8	3.39	Flexible, resilient, homogeneous cellular structure

The effect of the AS-2 surfactant concentration on the fatigue resistance of polyimide foams was extensively studied in NAS9-15484 (Ref. 3) for three different candidates including the 1720-1 flexible foams. The foams were produced at AS-2 concentrations of 0.1, 0.25, 0.5, 0.75, 1.0 and 1.5 percent. Of all the foam candidates subjected to fatigue in NAS9-15484, only four samples survived the 10,000 cycles requirement with a maximum loss of thickness of 20 percent. These candiates belonged to the 1720-1 series and were produced at an AS-2 concentration of 0.1, 0.25, 0.5, 0.75 percent respectively.

Because the surfactant concentration affects the most critical property of the foam, namely fatigue resistance, it was judged important to the success of this program to define the concentration of the AS-2 within the closest range possible before a final composition was selected. This effort was carried out in the last part of the present program by evaluating the fatigue properties of large foams produced in the 15 kW GFE oven at AS-2 concentrations of 0.5, 0.75 and 1.0 percent respectively and 2.5 percent blowing agent, using the fabrication process selected for the final prototype sample shipment. Summary of the data derived from this study is reported in Table 11.

The cellular structure of the foams reported in this table are very similar, but the number of visible flaws were higher at low AS-2 concentration. This was expected since high surfactant concentration reduces the surface tension of the expanding bubbles and facilitates the escape of the vapor from the cell walls uniformly.

Table 11

Effect of AS-2 Concentration on Critical Properties of Terpolyimide Foams Produced in the 15 kW Microwave Oven (GFE)

AS-2 Concentration	Blowing Agent (%)	Density		ILD (lbf)		Fatigue Thickness Loss (%)
		lb/ft^3	kg/m^3	25%	65%	
0.5	2.5	0.83	13.2	42.8	157	18.8
0.75	2.5	0.96	15.3	51.5	187	4.6
1.0	2.5	0.90	14.4	48.4	178	9.4

From the data reported in Table 11 the foams produced at 0.75 and 1.0 percent AS-2 respectively, appear to be similar in fatigue performance. The evaluation of properties carried out in Task III and IV was made on foams produced at a surfactant concentration of 1.0 percent. This concentration was changed in Task V and Task VI to 0.75 percent, because this type of foam exhibited a slight edge in fatigue properties.

4.2.4 Reactants Ratio

This effort involves the modification of the terpolymer resin system developed under NAS9-15484. The major objective of this task is to evaluate the effects of compositional changes upon the physical properties of the foam products by modifying the ratios of aromatic, heterocyclic and aliphatic diamines. These modifications were expected to result in resin compositions which would yield improved flexible foams and candidates with specific ILD values.

To accomplish this objective the task was divided into three subtasks listed below:

1. Evaluation of reactant ratios in the 5 kW microwave oven
2. Large scale foam evaluation of reactant ratios in the 15 kW GFE microwave oven
3. Optimization of the selected formulation made at a constant aliphatic diamine concentration of 0.16 mole/mole BTDA

Evaluation of Reactant Ratios in the 5 kW Microwave Oven

The work on this subtask is divided into three separate but complimentary schemes:

- Evaluation of polyimide precursors at constant heterocyclic diamine concentration
- Evaluation of polyimide precursors at constant aliphatic diamine concentration
- Evaluation of polyimide precursors at constant aromatic diamine concentration

The liquid resins for these studies were prepared in a 5.0 liter reactor and spray dried at an outlet temperature of 56-60°C (132.8-140°F). All foam samples were prepared in the 5 kW microwave oven at a power output of 2.5 kW at a loading of 1.0 kg. After microwave foaming, the foams were cured thermally for one hour at a temperature of 121-260°C (250-500°F). The results obtained from the evaluation of foam properties are summarized for each of the compositional scheme, as reported below.

Evaluation of Polyimide Precursors at Constant Heterocyclic Diamine Concentration

Each foam prepared as previously described was tested for the most critical properties, which included density, compression set and ILD values.

The results from this study are reported in Table 12. As shown, each foam was produced at a constant concentration of the heterocyclic diamine of 0.3 mole per mole of BTDA. The test data have been plotted for each of the critical properties against the aliphatic diamine variable and the graphs derived are shown in Figure 33 for effect on density, Figure 34 for effect on ILD values and Figure 35 for effect on the compression set values. Figure

Table 12

Ratio Study - Physical Properties of Polyimide Foams at Constant Heterocyclic Diamine Concentration

FOAM NUMBER	MOLE RATIO (DAP:MDA:DAH)	DENSITY		INDENTATION LOAD DEFLECTION (ILD)				COMPRESSION SET LOSS (%)		FOAM CHARACTERISTICS
				N		lbf				
		kg/m^3	lbs/ft^3	25%	65%	25%	65%	90	50	
56-1	0.3:0.58:0.12	10.3	0.64	100	342	22.5	77	37.5	12.4	Homogeneous
54-1	0.3:0.56:0.14	9.0	0.56	88	271	19.8	61	26.2	15.3	Homogeneous
48-2	0.3:0.54:0.16	14.4	0.90	86	289	19.3	65	40.0	12.6	Homogeneous
50-4	0.3:0.52:0.18	15.9	0.99	79	311	17.7	70	38.3	12.2	Homogeneous
50-3	0.3:0.50:0.20	12.2	0.76	101	338	22.8	76	39.0	11.9	Homogeneous
52-2	0.3:0.48:0.22	25.1	1.57	182	823	40.9	185	40.4	12.5	Reticulated Areas

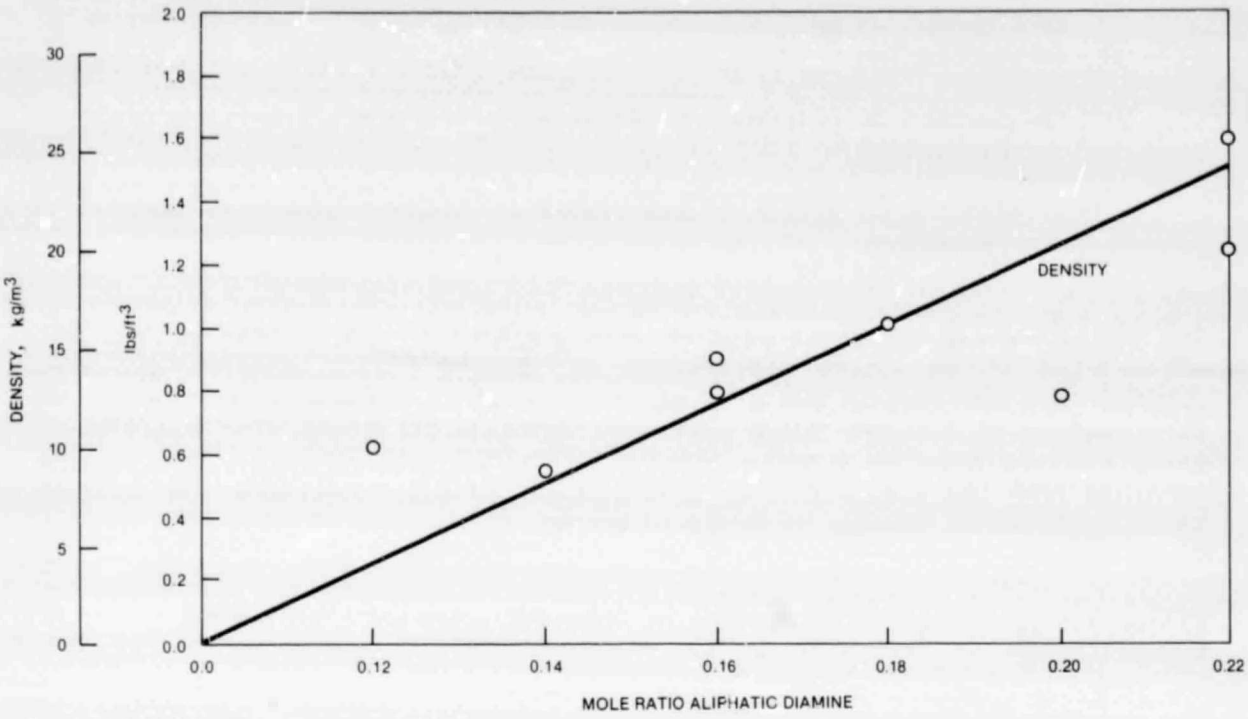


Figure 33. Effect of the Aliphatic Diamine Molar Concentration on Density of Terpolyimide Foams

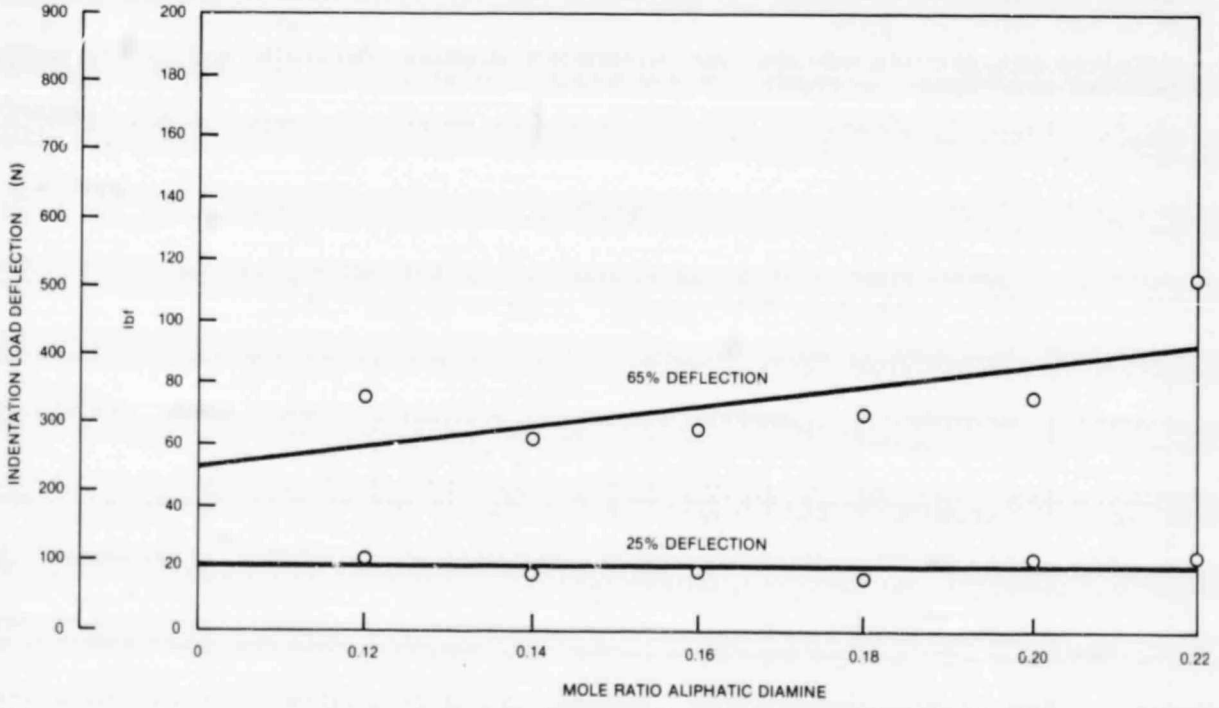


Figure 34. Effect of Aliphatic Diamine Molar Concentration on ILD Values of Terpolyimide Foams

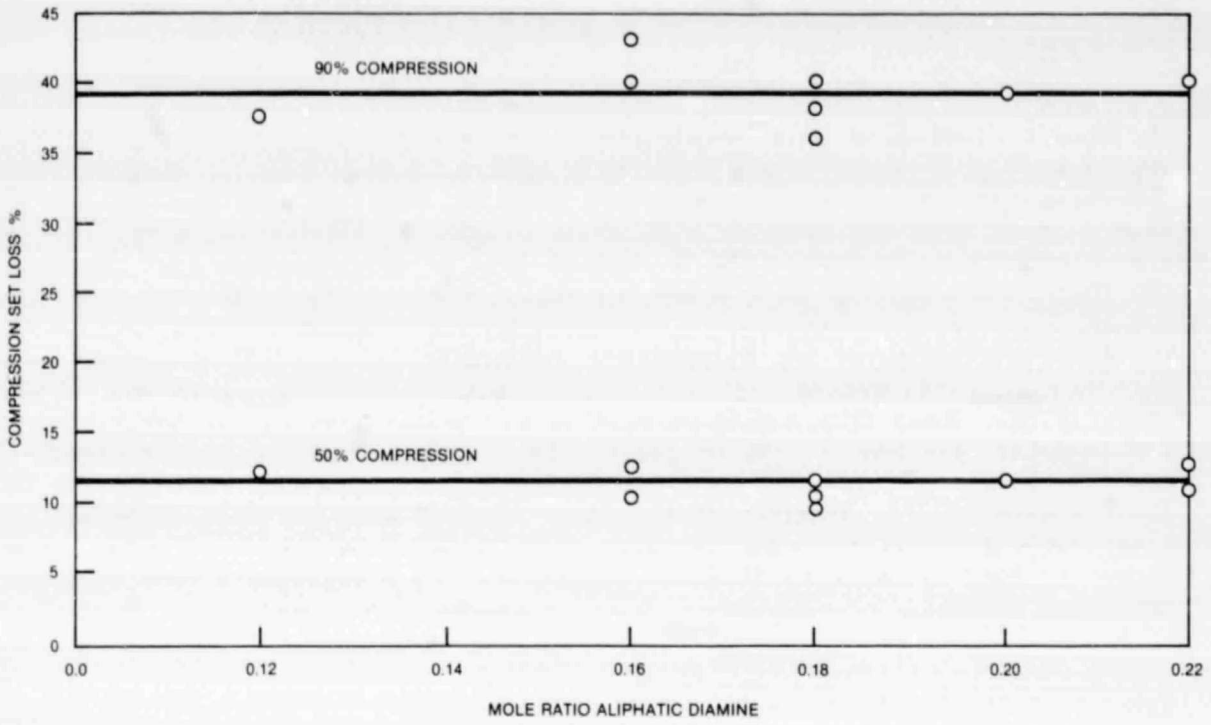


Figure 35. Effect of Aliphatic Diamine Molar Concentration on Compression Set Value of Terpolyimide Foams

33 clearly shows that precursor compositions made at increasing aliphatic diamine concentration produce foams with correspondingly higher density values. This direct relationship between density and concentration of aliphatic diamine is more a result of a higher level of foam collapse which occurs during curing than on the change of the molecular structure brought about by the chain lengthening effect of the aliphatic moiety. The increase in density should produce correspondingly higher ILD values. This effect is shown in Figure 34 where the ILD values at 65 percent deflection increase with increasing aliphatic diamine ratio. This same effect is not apparent for the ILD values at 25 percent deflection probably because of nonhomogeneous density distribution of the collapsed foams.

The compression set properties of the terpolyimide foams are independent of compositional changes as illustrated in Figure 35. This is true for compression set values at both 50 and 90 percent compression.

Precursor formulation derived from this study were selected for scale-up in this task, as discussed later.

Evaluation of Polyimide Precursors at Constant Aliphatic Diamine Concentration

The data derived from this compositional study are reported in Table 13 for two compositions only, since precursors made at a heterocyclic diamine concentration greater than 0.32 mole per mole of BTDA did not produce usable foams. Each foam was made at a constant aliphatic diamine concentration of 0.2 mole per mole of BTDA. Due to lack of data no relationships were derived. The foams produced from this study are illustrated in Figure 36.

The foaming behavior of the terpolyimde precursors is drastically altered when the reactant ratio exceeds certain limits. Studies carried out in NAS9-15484 (Ref. 3) have shown that a balance must be maintained between the heterocyclic and aromatic diamines to obtain quality foams. This balance was exceeded in the experiments carried out in this task when the precursors were made at or above a heterocyclic diamine concentration of 0.35 mole per mole of BTDA. At a heterocyclic diamine concentration of 0.38 mole per mole of BTDA, this effect is very dramatic as shown in Figure 36. No formulations were selected from this study.

Evaluation of Polyimide Precursors at Constant Aromatic Diamine Concentration

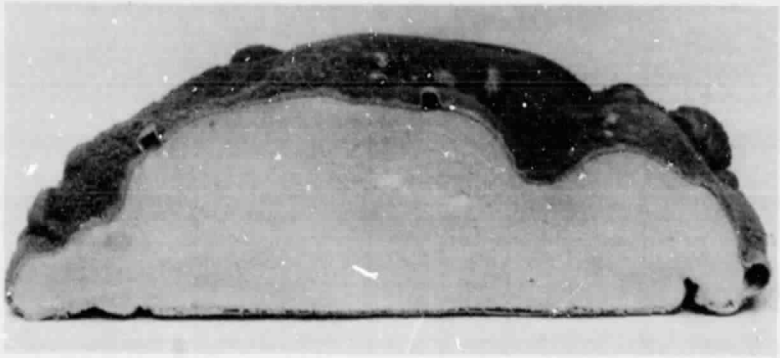
The data obtained from this ratio study are listed in Table 14. All foams were produced at a constant aromatic diamine concentration of 0.50 mole per mole of BTDA. The foams are illustrated in Figure 37 which shows the effect of increasing concentration of the heterocyclic diamine on the foaming behavior of the powder precursors.

As discussed previously, there is a range of ratios between the heterocyclic and aromatic diamines which must be maintained to obtain usable foams. This range can be changed if the concentration of the aliphatic diamine is decreased

Table 13

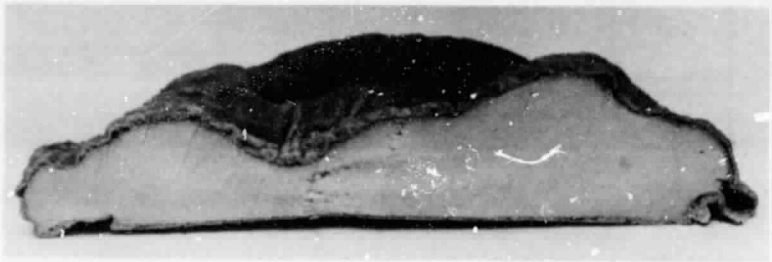
Ratio Study - Physical Properties of Polyimide Foams at Constant Aliphatic Diamine Concentration

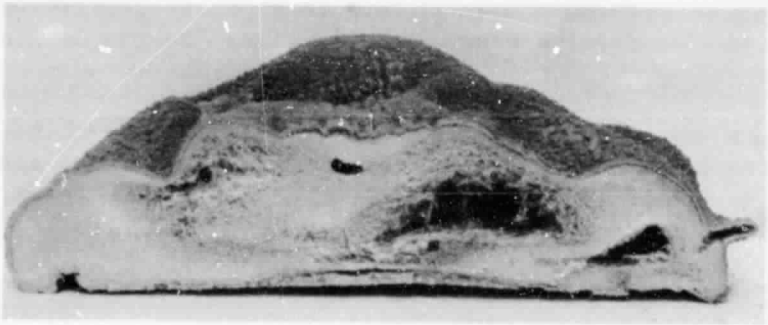
FOAM NUMBER	MOLE RATIO (DAP:MDA:DAH)	DENSITY		INDENTATION LOAD DEFLECTION (ILD)				COMPRESSION SET LOSS (%)		FOAM CHARACTERISTICS
				N		lbf				
		kg/m^3	lbs/ft^3	25%	65%	25%	65%	90	50	
82-3	0.32:0.48:0.20	10.9	0.68	99	360	22.3	81	38.1	12.0	Some Reticulation
83-4	0.34:0.46:0.20	17.8	1.11	157	765	35.4	172	20.2	12.7	Reticulated
84-5	0.36:0.44:0.20	--	--	--	--	--	--	--	--	Large Holes, Very Reticulated
85-6	0.38:0.42:0.20	--	--	--	--	--	--	--	--	Hollow Shell



A = 0.32, 0.48, 0.20

B = 0.34, 0.46, 0.20





C = 0.36, 0.44, 0.20

D = 0.38, 0.42, 0.20

Figure 36. Ratio Study - Polyimide Foams Derived From Precursors Made at Constant Aliphatic Diamine Concentration

Table 14

Ratio Study - Physical Properties of Polyimide Foams at Constant Aromatic Diamine Concentration

FOAM NUMBER	MOLE RATIO (DAP:MDA:DAH)	DENSITY		INDENTATION LOAD DEFLECTION (ILD)				COMPRESSION SET LOSS (%)		FOAM CHARACTERISTICS
				N		lbf				
		kg/m^3	lbs/ft^3	25%	65%	25%	65%	90	50	
88-2	0.32:0.50:0.18	13.0	0.81	68	388	15.2	87.4	35.3	11.2	Homogeneous
89-3	0.34:0.50:0.16	10.7	0.67	45[1]	304	10.1[1]	68.3	37.8	13.9	Slightly Reticulated
90-4	0.36:0.50:0.14	14.3	0.89	140	729	31.7	164	33.1	12.4	Holes, Reticulated
91-5	0.38:0.50:0.12	10.7	0.67	81	151	18.2	33.9	30.3	12.3	Holes, Reticulated

NOTE: 1. Sample was reticulated over 1/2 its area.

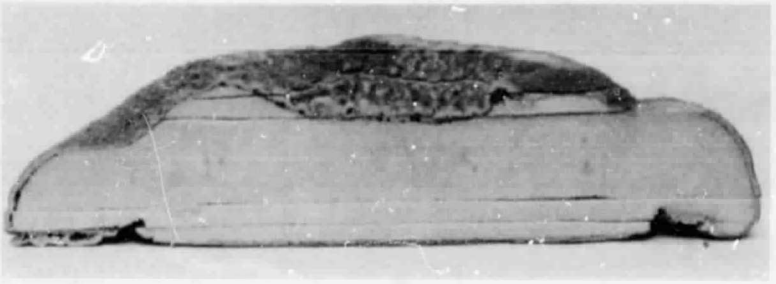
to 0.16 mole/mole of BTDA. As shown in this study, this change permits the use of higher concentrations of the heterocyclic diamine than previously possible.

Evaluation of the physical properties reported in Table 14 failed to yield any firm relationships. This was probably due to the excessive amount of reticulation found in the foams. Because of this deficiency, the foams were neither homogeneous in cellular structure nor uniform in physical properties within the bun, thus giving varied results depending upon where the sample was taken.

This effort did not produce any breakthrough in polyimide technology but helped to clarify the foaming behavior of certain terpolyimide precursors and to more clearly identify the limits of each reactant to yield usable foams.

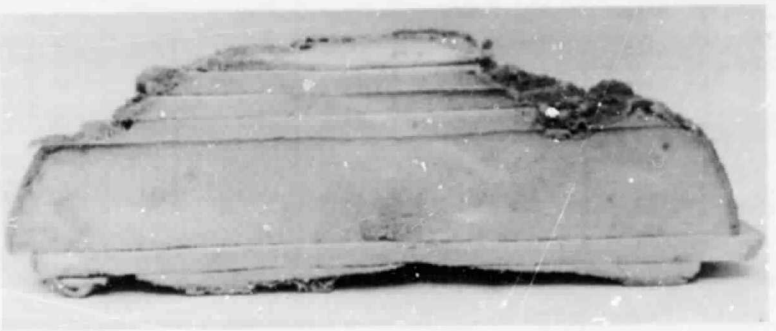
Large Scale Evaluation of Foams Produced From Precursors Made at Various Reactant Ratios in the 15 kW GFE Microwave Oven

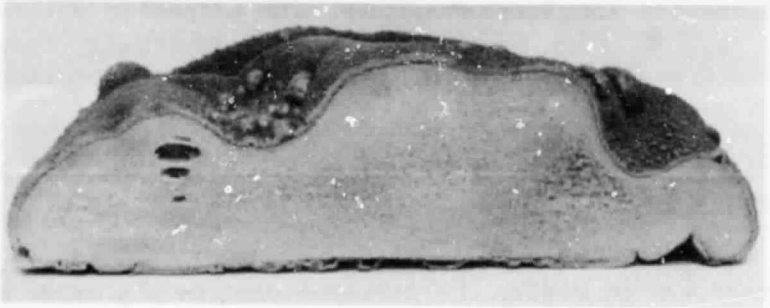
As discussed previously, polyimide precursor formulations made at constant heterocyclic diamine concentration were selected for scale-up in this task. These were foamed in the 15 kW GFE microwave oven at a power ratio of 0.84 kW/kg using a blowing agent concentration of 2.5 percent. The formulations studied and the test results obtained are listed in Table 15. Examination of the data yields no definite trends as was previously shown to be the case for foams made in the 5 kW oven. This study again demonstrates that compositional changes have no significant effect on the foam properties. Two important characteristics were uncovered in this study and involved foam collapse which decreased with lower aliphatic diamine ratios and the fatigue resistance of the foams which improved with increasing aliphatic diamine concentration. These two features quickly became important considerations during selection of the most promising reactant ratio. After considering



A = 0.32, 0.50, 0.18

B = 0.34, 0.50, 0.16





C = 0.35, 0.50, 0.14

D = 0.38, 0.50, 0.12

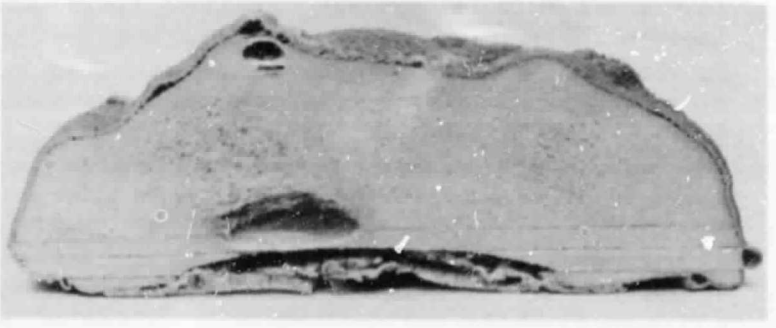


Figure 37. Ratio Study - Polyimide Foams Derived From Precursors Made at Constant Aromatic Diamine Concentration

Table 15

Ratio Study - Physical Properties of Polyimide Foams at a Constant Heterocyclic Diamine Concentration (15 kW Oven)

Foam Number	Mole Ratio	Density		Indentation Load Deflection (ILD) N		Indentation Load Deflection (ILD) lbf		Compression Set Loss (%)		Fatigue Loss (%)
		kg/m^3	lbs/ft^3	25%	65%	25%	65%	90%	50%	
207M	0.3:0.7:0.0	11.4	0.71	141	698	31.7	157	51.6	17.6	22.5
203M	0.3:0.6:0.1	10.3	0.64	112	394	25.3	88.6	42.5	18.6	25.6
199M	0.3:0.58:0.12	13.7	0.85	144	516	32.4	116	54.1	18.5	10.1
201M	0.3:0.56:0.14	11.6	0.72	157	582	35.4	131	37.4	14.1	5.4
187M	0.3:0.54:0.16	15.4	0.96	207	760	46.5	171	45.0	10.6	3.4
145	0.3:0.52:0.18	18.0	1.12	169	556	38.0	125	48.5	11.7	NA
146	0.3:0.50:0.20	14.8	0.92	225	653	50.6	147	43.7	10.9	NA

Note 1: NA - not available.

the problem of collapse, the data given in Table 15, and after visual observation of foaming characteristics and foam structure, the aliphatic diamine concentration was lowered to 0.16 mole/mole BTDA and all subsequent foams were produced from precursors made at this aliphatic diamine concentration.

Optimization of the Selected Formulation Made at a Constant Aliphatic Diamine Concentration of 0.16 Mole per Mole of BTDA.

The objective of this subtask was to modify the selected formulation, made at an aliphatic diamine concentration of 0.16 mole per mole of BTDA and to define the optimum ratio of aromatic and heterocyclic diamine. These preliminary experiments were carried out in the 5 kW microwave oven. The results derived from these formulations are listed in Table 16 and the foams shown in Figure 38. Heterocyclic diamine concentrations of less than 0.30 mole/mole BTDA produced no detectable improvements in ILD or compression set. At concentrations greater than 0.30 mole/mole BTDA the foams became more reactive in the microwave field resulting in increasing reticulation which led to collapse. The formulation selected previously, made at a ratio of 0.30:0.54:0.16, was again found to exhibit the optimum foam properties.

In this task it was found that moderate compositional changes do little to effect ILD or compression set, however these changes produced foam collapse which resulted in non-uniformity of physical properties. Based upon these findings, foams produced from precursors made at a ratio of 0.30:0.54:0.16 were found to possess the optimum foam properties and were selected for all subsequent studies including the production of the final prototype samples for evaluation by NASA-Johnson Space Center.

Table 16

Ratio Study - Physical Properties of Polyimide Foams at a Constant Aliphatic Diamine Concentration (0.16 Mole/Mole BTDA)

Foam Number	Mole Ratio	Density		Indentation Load Deflection (ILD) N		Indentation Load Deflection (ILD) lbf		Compression Set Loss (%)		Comments
		kg/m^3	lbs/ft^3	25%	65%	25%	65%	90%	50%	
95-5	0.26:0.58:0.16	14.0	0.87	142	442	31.6	98.2	59.7	12.7	Homogeneous
95-6	0.28:0.56:0.16	30.8	1.92	205	1076	45.5	239	41.6	10.8	Homogeneous
48-2	0.30:0.54:0.16	14.4	0.90	87	293	19.3	65.1	40.0	12.6	Homogeneous
96-7	0.32:0.52:0.16	18.0	1.12	163	711	36.3	158	39.0	11.1	Very Slight Reticulation
89-3	0.34:0.50:0.16	10.8	0.67	45	307	10.1[1]	68.3[1]	37.8	13.9	Slight Reticulation
96-8	0.36:0.48:0.16	24.4	1.52	256	1035	56.8	230	40.7	10.5	Very Dense, Reticulated Areas
100-9	0.38:0.46:0.16	--	--	--	--	--	--	--	--	Collapsed
100-10	0.40:0.44:0.16	--	--	--	--	--	--	--	--	Collapsed
100-11	0.42:0.42:0.16	--	--	--	--	--	--	--	--	Collapsed

Note 1: Testing sample contained a reticulated area.

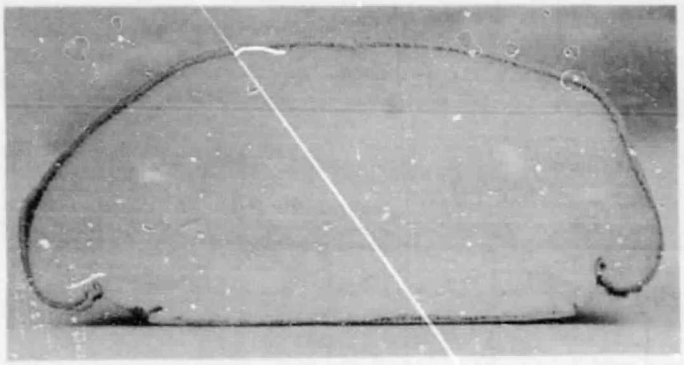
4.2.5 Quality Standards

The objective of this task was to establish quality control measures to aid in the consistent production of polyimide foams possessing specific ILD and density characteristics.

The task is divided into five sections. Sections I and II deal with the measures established to assure the quality of raw materials and liquid polyimide precursors respectively. Section III deals with the quality standards of polyimide powder precursors and additives where as Section IV deals with the finished polyimide foams. In Section V, an attempt is made to correlate important quality parameters to foaming behavior and foam properties.

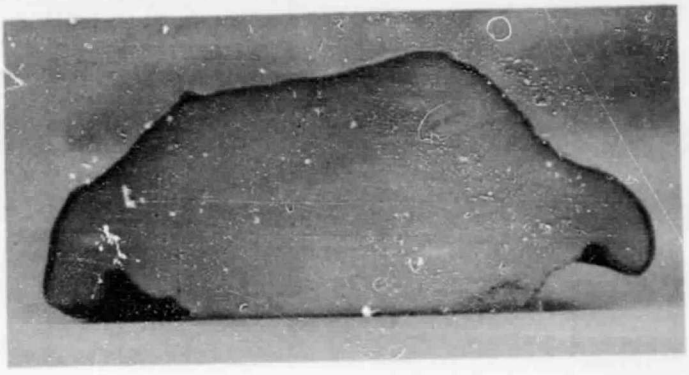
Raw Materials

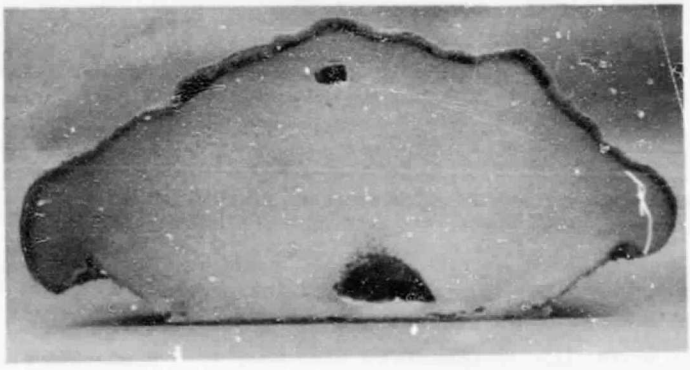
The parameter selected to establish quality control of major raw materials used in the synthesis of liquid polyimide precursors was melting point. Melting point determinations for the raw materials was carried out in a 6406-H Thomas-Hoover Melting Point apparatus using raw material samples taken from the bottom, middle, and top of the shipping container.



Foam 1 - 0.26:0.58:0.16

Foam 2 - 0.28:0.56:0.16





Foam 3 - 0.32:0.52:0.16

Foam 4 - 0.34:0.5:0.16

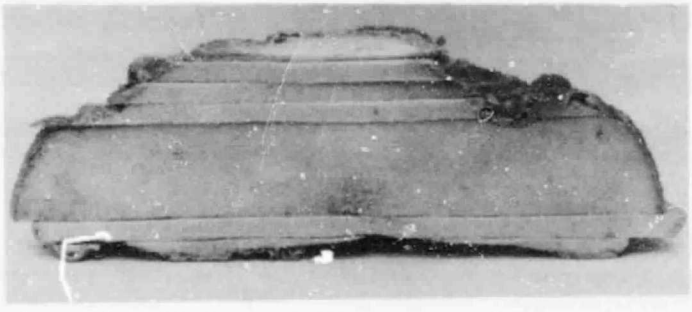
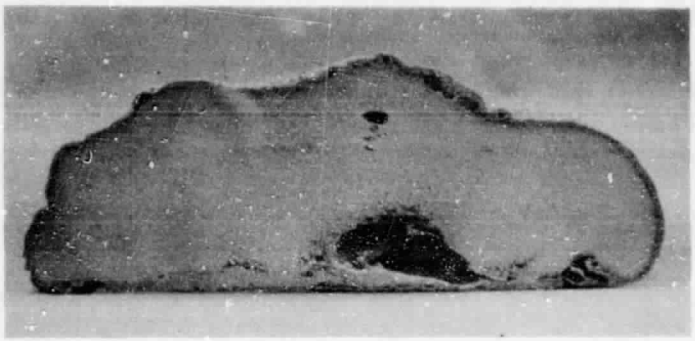
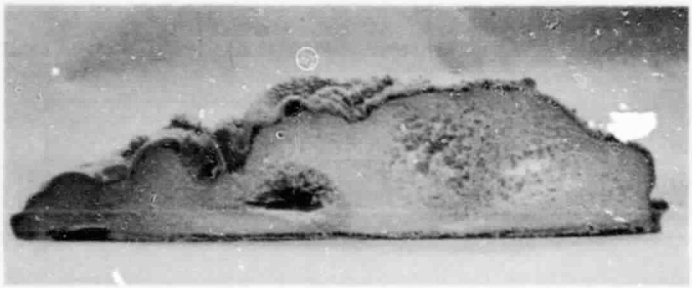


Figure 38. Ratio Study - Polyimide Foams Derived From Precursors Made at a Constant Aliphatic Diamine Ratio of 0.16 Mole/Mole BTDA (Sheet 1 of 2)

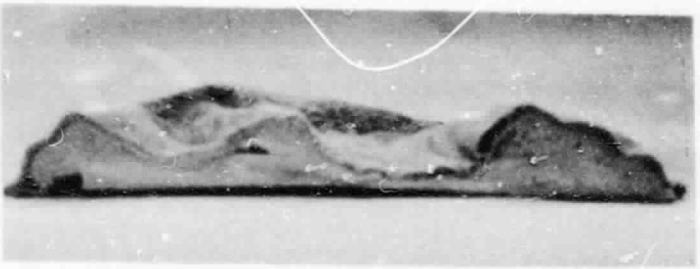


Foam 5 - 0.36:0.48:0.16

Foam 6 - 0.38:0.46:0.16



Foam 7 - 0.40:0.44:0.16



Foam 8 - 0.42:0.42:0.16

Figure 38. Ratio Study - Polyimide Foams Derived From Precursors Made at a Constant Aliphatic Diamine Ratio of 0.16 Mole/Mole BTDA (Sheet 2 of 2)

The analysis of all major raw materials was carried out periodically by Infrared Spectroscopy obtained by the KBr pressed wafer method on a Beckman Model 1R8 infrared spectrophotometer. All liquid raw materials were analyzed by measurement of the specific gravity and by visual inspection.

The melting point and IR spectrum of the major raw materials are reported in Section 3.

Liquid Polyimide Precursor

The parameter selected for the quality control of the liquid polyimide precursor was viscosity of liquid resin. Viscosity determinations for the liquid resin were carried out by Zahn Viscosimeter. Since the temperature is known to affect the viscosity of a liquid, a viscosity temperature curve was established as shown in Figure 39.

The viscosity measured by the Zahn viscosimeter is expressed in Zahn seconds, that is, the time required for a definite volume of liquid to flow through the orifice in the bottom of a metal cup. In all the experiments, Zahn cup #1 was used.

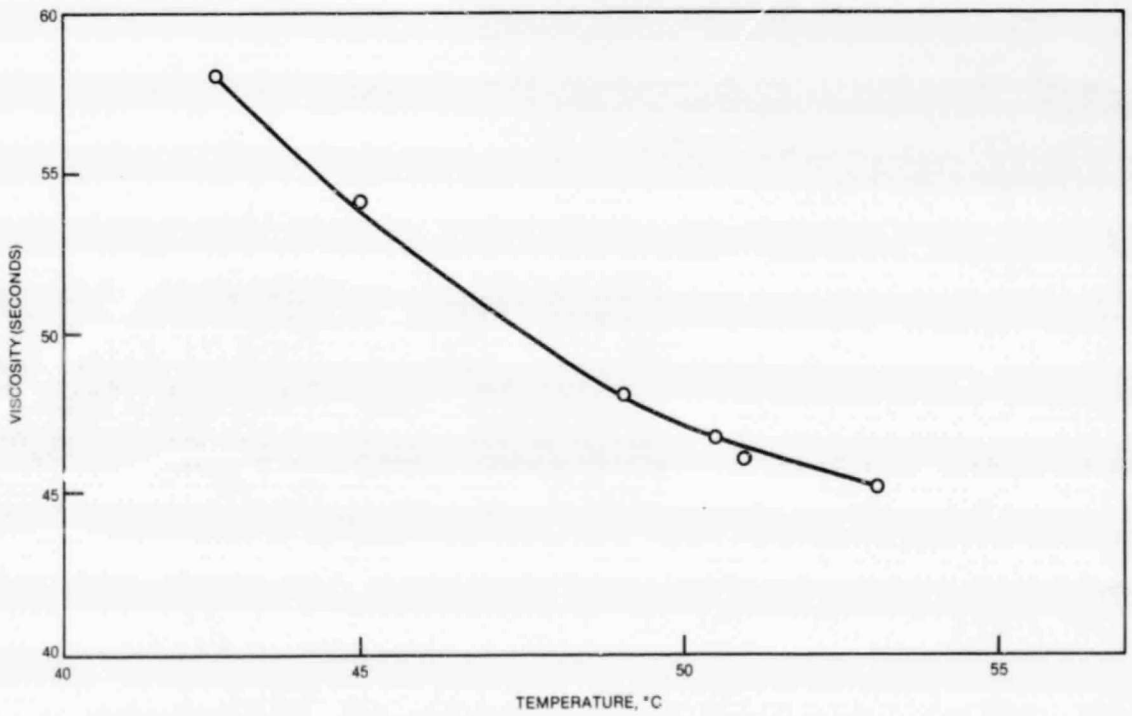


Figure 39. Viscosity-Temperature Relationship of Polyimide Liquid Precursor

The liquid precursors which did not meet the viscosity requirements at the temperatures reported in the graph were rejected. In addition to viscosity measurements, the liquid resin was checked for foaming behavior at 500°F. In this test the foam rise and foam quality was checked against a standard. Liquid precursors which did not meet this standard were abandoned.

Powder Precursors and Additives

The parameters selected for the control of the quality of the powder precursors and additives were the particle size distribution, volatile content, and foaming behavior. To assure consistent distribution of particle size, standard distribution curves have been established for the powder precursor at various spray dryer outlet temperatures. These curves are shown in Figure 40. The powder precursors were tested to meet this requirement before being processed. The foaming process is aided by the use of a blowing agent, Celogen HT 550, which is added and mixed with powder precursors prior to foaming. Standard particle size distribution curves for this additive have also been established at various ball milling hours. These curves are shown in Figure 41.

Since the particle size of the blowing agent was found to control the cell size of the finished foams, the distribution curve for each batch of the blowing agent was compared against the standard curve before use.

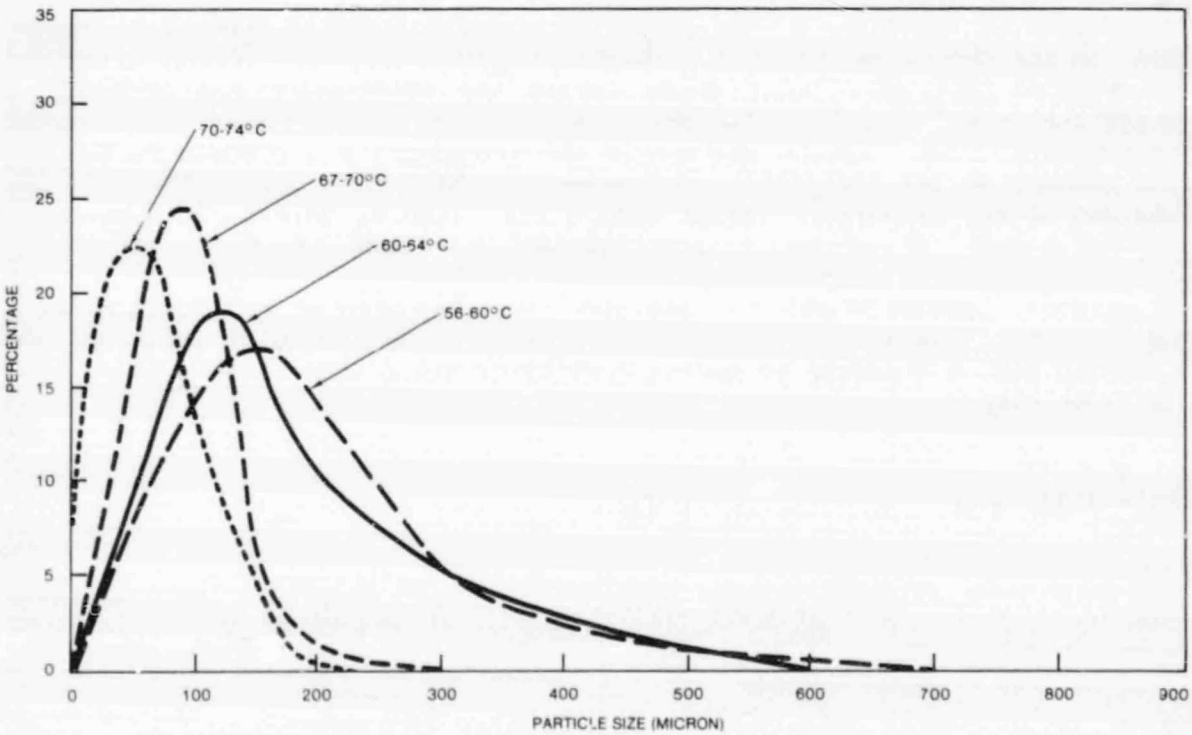


Figure 40. Particle Size Distribution of Powder Precursors - Spray Dryer Outlet Temperature Study (Inlet = 100°C)

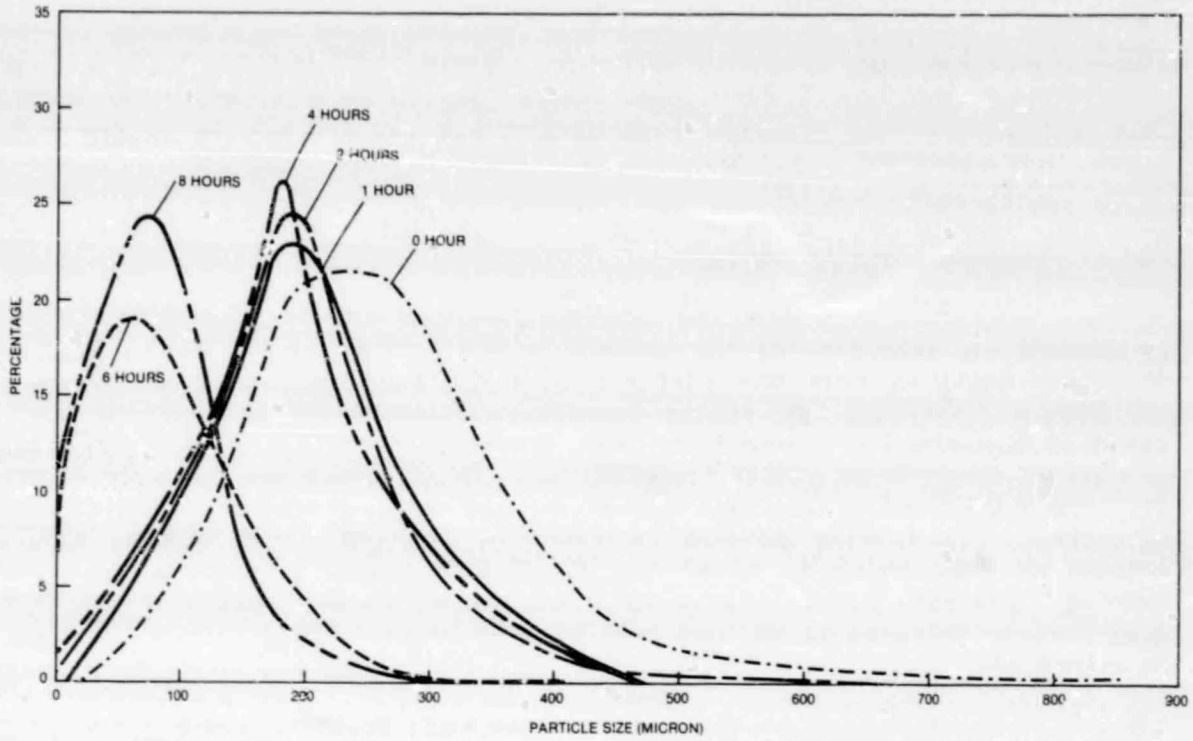


Figure 41. Standard Particle Size Distribution Curves for Blowing Agent (Celogen HT 550)

The degree of expansion of the polyimide precursors during foaming is dependent on the concentration of the volatiles. The volatile content, a mixture of methanol and water that forms during the amidization and imidization reactions is a function of the spray drying process and depends on the drying temperature. The volatile content of the precursors was checked by heating the powders at 287.7°C (550°F) and measuring the weight loss. The volatile content of the precursors varies within the range of 20.0 to 20.5 percent. Any batch that did not meet this requirement was abandoned.

Finally the foaming behavior of the precursors was checked by foaming a 100 g batch in the 5 kW microwave oven. The foam rise and cellular structure was compared with a standard to assure quality of the powders before foaming in large batches.

Polyimide Foams

The parameters selected for the quality control of polyimide foams included density, indentation load deflection values at 25 and 65 percent deflection, compression set loss values at 30, 50, 70 and 90 percent compression, and fatigue loss at 8,000 cycles.

The quality control procedure involved obtaining representative test samples from the large foams produced in the 15 kW microwave oven. A schematic of

large foam cut up for testing samples is shown in Figure 42. The tests were carried out according to ASTM methods reported in Section 3, Experimental Procedures. The results of these tests were used to define relationships between processing parameters and foam properties and in evaluating uniformity within and between buns. The same tests and additional quality standards were also used to prepare final specifications for each of the five classes, selected in the following tasks.

Correlation of Quality Parameters to Polyimide Foam Properties

The quality of the raw materials has been found to be a major factor contributing to variability of foam properties under identical processing conditions. Of all the raw materials used, the dianhydrides were found to vary from batch to batch more than any other raw materials purchased. This quality problem was resolved by washing the dianhydrides with acetone to remove impurities contributing to lower melting point. The powder precursors obtained by using raw materials meeting quality standards produced foams which possessed uniformity of cellular structure only if the temperature of the spray drying process was maintained constant within very close limits. This dependancy was uncovered during this work and was attributed to the effect of the temperature of the spray dryer on the particle size of the powder precursors, the higher the temperatures the finer the particle size. Larger particle sizes were found to absorb more energy in an electromagnetic field resulting in foams with nonhomogeneous density and ILD characteristics. The temperature of the spray dryer has also shown to control the volatile content of the precursors and hence influences the foaming behavior.

Similarly, the particle size of the blowing agent was controlled within very close range to assure uniformity of cellular structure. Large particle size produces a wide variation in cell size and nonuniform density distribution within and between foams. More importantly, the concentration of the blowing agent was found to affect the foaming behavior of the precursors and to alter the cellular structure of the foams.

It was during the execution of this task that two processing parameters were found to produce changes to the density and ILD properties of the foams. These parameters are the temperature of the spray dryer and the concentration of the blowing agent. The development of these relationships was later used to generate conditions to produce polyimide foams with different ILD characteristics, which were further classified into five classes in accordance with predetermined values of the ILD at 25 percent deflection.

4.2.6 Testing and Selection

This task, which was carried out concurrently with each of the subtasks discussed above, entails evaluation of polyimide foams through the process of iterative testing for mechanical properties such as density, compression set, modulus, ILD, and comfort index. This subtask was planned out to screen prom-

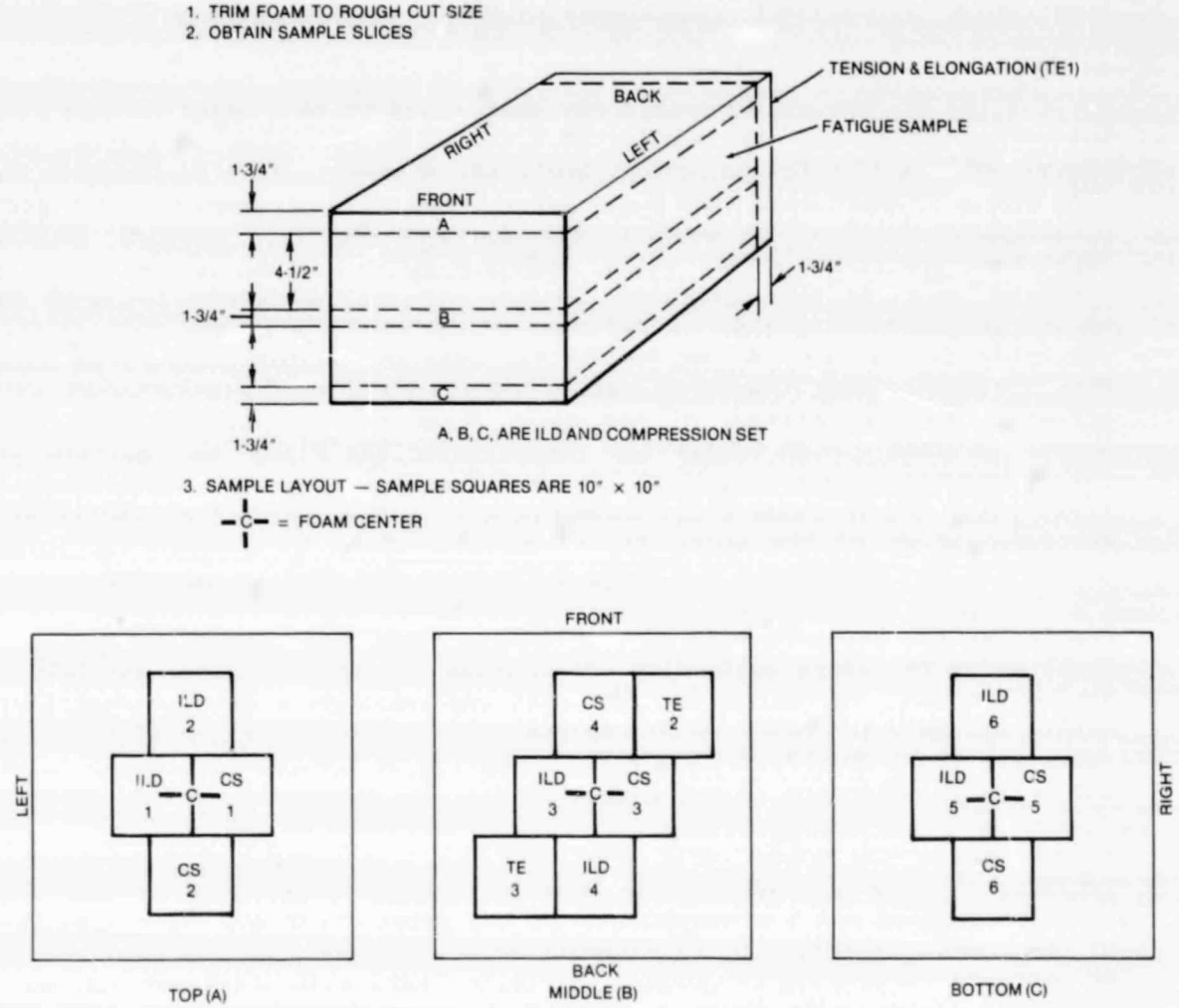


Figure 42. Sampling Schematic for Testing

ising candidates and establish several classes of polyimide foams, each meeting a specified value of ILD at 25 percent deflection.

The first step of this task was carried out by preparing the powder precursors in a five-mole batch size followed by foaming the powders in the 5 kW Model 4115 microwave oven. The foams were then evaluated for cellular homogeneity and structure and candidates selected for further scale-up.

In a second step these candidates were scaled-up to a twenty-mole batch size and the powder precursors foamed in the 15 kW GFE microwave oven. Testing of the foams started with the most critical properties which included density, ILD at 25 and 65 percent, and compression set at 50 and 90 percent. Evaluation of the fatigue strength and resistance of the foams to humid environments was carried out with specific foams only to determine the effect of certain compositional changes.

In most cases, testing was carried out to establish relationships between process parameters or compositional changes and foam properties and to screen the factors which contributed to specific levels of ILD values at 25 percent deflection. Table 17 shows the relationship between outlet temperature of the spray drying process and the properties of the powder precursors and their respective foams.

Table 17

Testing and Selection - Interrelations of Terpolyimide Foam Properties

	POWDER				FOAM						
OUTLET TEMP. °C	YIELD kg/h	BULK DENSITY g/cc	MEAN PARTICLE SIZE microns	% VOLATILE	DENSITY kg/m³	ILD 25% lbf	ILD 25% N	ILD 65% lbf	ILD 65% N	C.S. 50%	C.S. 90%
56-60	3.36	.351	140	22.3	17.6	42.6	189.5	153.8	684.1	8.7	34.9
60-64	3.18	.316	120	21.7	19.6	43.3	192.5	136.3	606.2	9.2	42.3
67-70	2.27	.295	98	20.7	24.1	63.2	281.1	216.8	964.3	12.9	43.9
70-74	1.72	.280	76	19.2	25.6	99.5	442.5	442.5	1968.2	12.8	49.9

As clearly demonstrated by the data, a high outlet temperature causes a decrease of the powder precursors yield brought about by the low feed rate of the liquid resin required to maintain the proper heat balance in the drying chamber. Lower feed rate produces finer liquid atomization and precursors possessing smaller particle size, low bulk density and low volatile content. The effect of the precursor properties on the respective foams is also clearly shown in Table 17.

The density of the foams increases as the particle size of the precursors decreases. Higher densities produce correspondingly higher ILD values. The effect of these process parameters on the ILD values are clearly understood

since foam deflection properties and densities are directly related, but the effect on the compression set is less explainable.

The ILD values of all the foams tested in this phase of the program were plotted against their respective densities and the results are shown in Figure 43. These data were plotted without filtering results considered to be deviating from the normal.

The data reported in Table 17 display outlet temperature conditions which produce foams with ILD values meeting the requirements for three of the five classes established in this program. These three classes have ILD values at 25 percent deflection of 99.5, 63.2 and 43.3 lbf respectively.

Foams produced at different outlet temperatures were tested for resistance to humid environments at 74°C (165°F) and 100 percent relative humidity for a period of seven days. These foams were produced in a 15 kW GFE microwave oven at a power ratio of 1.3 kW/kg and cured for 42 minutes at 15 kW followed by thermal curing for 95 minutes at 350-475°F. Results of this test are summarized in Table 18.

The effort carried out during the task dealing with blowing agents resulted in the selection of Celogen HT 550 as the final candidate. The scale-up of this additive was successfully carried out in a 15 kW GFE microwave oven as

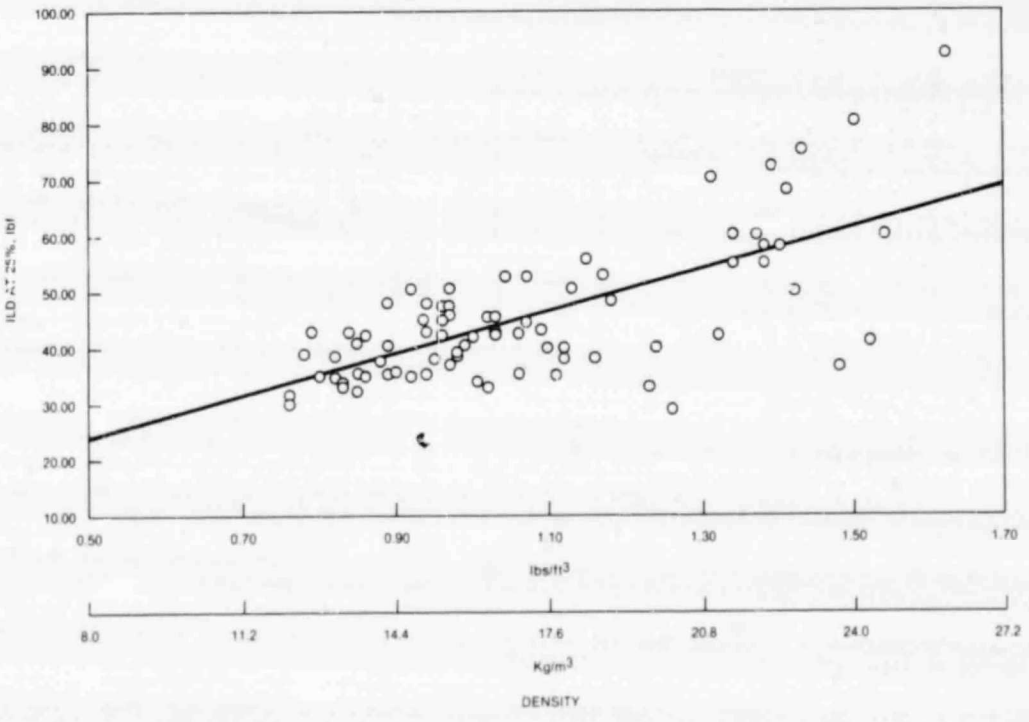


Figure 43. Terpolyimide Foams - Density-ILD Relationship

Table 18

Hydrolytic Stability of Terpolyimide Foams

Foam Number	Concentration of Blowing Agent (%)	Outlet Temperature (°C)	Density		Weight, g		ILD, lbf				Percent Loss	
							Before		After			
			kg/m^3	lbs/ft^3	Before	After	25%	65%	25%	65%	25%	65%
206	0.5	59±1	16.3	1.02	18.0	18.0	56.2	185	54.7	181	2.7	2.2
183	0.5	64±1	17.0	1.06	18.8	18.8	54.7	182	57.2	175	-4.6	4.2
220	0.5	69±1	22.4	1.40	25.9	25.8	74.9	253	74.9	256	0	-1.0
291	0.5	74±1	26.1	1.63	29.1	29.3	92.6	420	107.5	468	-16.1	-11.4

described in Section 4.2.2. Results indicate a definite relationship between concentration of blowing agent and ILD values of the polyimide foams.

Theoretically, polyimide foams possessing ILD values between the range of 21-85 lbf can be obtained by suitable selection of the concentration of the blowing agent and power ratio between the ranges of 0 to 7.5 percent and 1.0 to 1.3 kW/kg respectively. In addition, this range of ILD values can be expanded by proper choice of outlet temperature between 56-74°C. This concept will be further elaborated in Task III by iterative permutation of three important parameters, namely power ratio, concentration of blowing agent and outlet temperature.

The work on additives and fillers did not produce any viable candidates for classification.

The re-evaluation of best surface active agent, AS-2, developed under NAS9-15484, has shown dependence beween AS-2 concentration and ILD values of foams made in the 5 kW microwave oven. Concurrent with this study, Celogen HT 550 was selected as a blowing agent through a separate effort of Task II. When this blowing agent was introduced into the foaming process in the 15 kW microwave oven, the dependence of AS-2 concentration on ILD values was lost due to the predominant effect of blowing agent on density and ILD values. The effect of the concentration of blowing agent on ILD values of the terpolyimide foams produced in an open mold is fully described in Section 4.2.2.

The effect of compositional changes on the ILD values is reported in Table 19 for foams made in 5 mole batches and foamed in the 5 kW Model 4115 microwave oven. The data show that the ILD values of the terpolyimide 1720-1 foams are independent of the aliphatic diamine ratio over the range reported, and no classification into groups is attainable through compositional changes. These results confirmed the data derived from previous work (Ref. 3) which shows no correlation between precursor compositions and the ILD values of the foams.

The ILD values shown previously in Table 18 were obtained from foams produced in the 15 kW GFE microwave oven using the conditions established in Task I and those in Table 19 from foams produced in the 5 kW Model 4115 microwave oven using optimized process parameters developed in previous programs. The operating parameters of the two microwave ovens in addition to size and processing time are significantly different and affect the values of the ILD and compression set of the foams. The important conclusion of this study is the need to develop more advanced foam fabrication techniques which more closely reflect the conditions of the 5 kW microwave oven. This study is described in Task III in accordance with the plan.

Task II - Formulation and Optimization - Summary

The following brief review describes the major developments resulting from the experimental work carried out in Task II, Formulation and Optimization.

Table 19

Testing and Selection - Effect of Molar Ratio of the Aliphatic Diamine on ILD Properties of Terpolyimide Foams

Aliphatic Diamine Mole Ratio	ILD			
	25 Percent		65 Percent	
	lbf	N	lbf	N
0.12	22.5	100.0	77.0	342.5
0.14	19.8	88.0	61.0	271.3
0.16	19.3	85.8	65.1	289.5
0.18	17.7	78.7	69.5	309.1
0.20	22.8	101.4	76.0	338.0

1. A square open mold configuration with bottom grid and corner vents for release of vapors and polyimide insulation for improved curing has been selected for all foaming studies.

2. The ILD values of polyimide foams change proportionately with changes of the outlet temperature. Foams with ILD values of 99.5, 63.2, and 43.3 lbf were obtained at outlet temperatures of 70-74, 67-70 and 60-64°C, respectively.

3. A blowing agent, Celogen HT 550, was selected to produce more uniform cellular structure. It also permits changes in ILD values of the foams when its concentration is varied within the range of 0.25 to 7.5 percent.

4. Additives and fillers did not produce detectable changes in foam properties, particularly ILD values.

5. Re-evaluation of the best surface active agent, AS-2, did not show any relationship with ILD values. However, foams produced between 0.5 to 1.0 percent AS-2 have met the requirements of fatigue strength.

6. The data derived from the work carried out on compositional changes show that ILD values of the polyimide foams are independent of the aliphatic diamine ratio over the range reported and no classification into groups is attainable.

7. Quality standards have been established for raw materials, liquid and powder precursors, additives and polyimde foams.

8. At the end of Task II, three parameters were identified as most critical in classifying foams into groups according to ILD values; these are outlet temperature, concentration of the blowing agent, and power ratio.

4.3 TASK III - OPTIMIZATION OF FOAMING PARAMETERS

The major objective of this task is the optimization of processing parameters and foaming techniques to achieve foams with specific densities and multiple levels of comfort and durability not possible through Task I and Task II. The secondary objective of this task is to define the deficiencies, if any, of the present foaming techniques for prototype production samples.

4.3.1 Molding Techniques

Polyimide precursors are free flowing powders which evolve 19-22% volatiles and expand into a cellular structure when heated in a microwave cavity.

The polyimide foams discussed in Task I were produced exclusively by the free-rise technique. This method was chosen because it offered the least resistance to the escape of these volatiles. After the microwave processing, the foams were subjected to a thermal curing cycle to achieve resiliency and flexibility through the mechanism of a condensation polymerization reaction. The curing temperature was in the range of 218-288°C (425-550°F) which is so close to the glass transition temperature (285°C, 545°F) that softening of the material occurs. The deficiency of the free-rise foaming technique rests with the fact that the sides of the foam provide little or no support for the foam when it is heated to the softening point. This results in foam collapse. The effect of foam collapse is a variation of the density within the bun which consequently affects all other critical foam properties making it difficult to achieve reliable and reproducible classification into groups.

A solution to this problem has been found by foaming polyimide powder precursors and allowing the foaming mass to conform to the shape of the mold. Limited effort in this area was expended in NAS9-15484 and results of this study were described in the final report (Ref. 3). Perforated molds produced more homogeneous cellular structure with less flaws than closed molds, but both techniques were less adaptable to prot type large scale production than the free or vertically constrained rise techniques. It was noted that volatiles which remain entrapped in the mold produce large flaws and imperfections. This deficiency was also reported in Task I of the present program which will be the subject of the development work described next.

The work carried out in this task started with the fabrication of two large molds having dimensions of 91.5 x 91.5 x 61 cm (36 x 36 x 24 in.) and 122 x 122 x 91 cm (48 x 48 x 36 in.) respectively. The molds were fabricated with a 2.5 cm (1 in.) deep grid installed at the bottom with corner vents to allow for the escape of volatiles. The 122 x 122 x 91 cm (48 x 48 x 36 in.) mold is shown in Figure 44. The size of the mold was such that it just cleared the microwave door and the mode stirrer which is barely visible in Figure 45 where the same mold is shown in the 15 kW microwave oven on the aluminum rods and polyimide insulating foam supports.

The first series of experiments was carried out in the 91.5 x 91.5 x 61 cm (36 x 36 x 24 in.) mold at a loading of 10.0 kg and microwave power ratio of

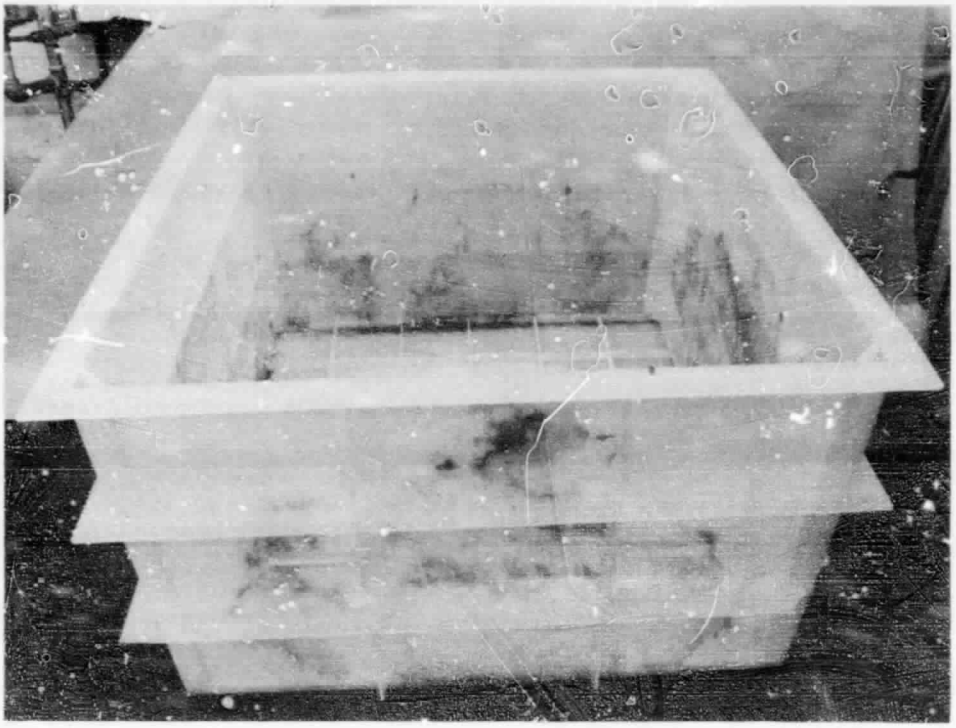


Figure 44. Polypropylene Mold Modified With Bottom Grid and Corner Vents

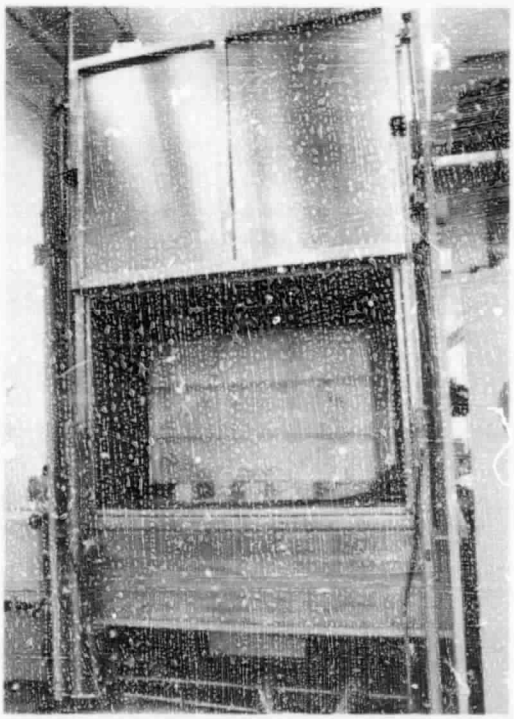


Figure 45. Mold Foaming Assembly in the 15 kW Microwave Oven

0.84 kW/kg. These experiments were designed to yield standard procedures for mold foaming prior to the start of parametric studies to evaluate the influence of processing on the cellular structure, homogeneity, uniformity, and physical properties such as density, compression set, and ILD values. These experiments produced process improvements and a reasonable level of foam yield (15%) to justify the parametric study. These process improvements are listed below.

1. Use of polyimide foam insulation liners for the sides of the mold to prevent heat loss and reduce the amount of secondary thermal foaming.

2. Lower support platform in the microwave cavity to prevent damage to the foam by the mode stirrer.

3. More consistent methods of powder lay-up by using shaped forms to control size and thickness of the powder beds to about 52 x 52 x 11.4 cm (20.5 x 20.5 x 4.5 in.).

4. Improved mechanical means of removal of the buns from the mold using Teflon coated glass strips installed in the mold itself.

The first effort of this parametric study involved the evaluation of the optimum loading to attain complete mold filling and best bun shape for maximum yield. The mold shown in Figure 44 (48 x 48 x 36 in.) was used in these experiments and foaming carried out at a pulsing cycle of 20 seconds ON and 20 seconds OFF.

Figure 46 shows the foams obtained from powder loadings of 10, 15 and 20 kg respectively (22, 33 and 44 lbs) using microwave power output ratios of 0.84, 0.71 and 0.625 kW/kg respectively.

Experiments 132M, at a loading of 10 kg (22 lbs) and to a lesser extent 133M, at a loading of 15 kg (33 lbs) did not produce complete mold filling, therefore some of the collapse characteristics of free-rise foaming were evident. When complete mold filling was attained, the foam conformed to the shape of the mold, and produced geometrically shaped buns almost identical to the configuration of the mold. The same figure shows the increasing foam rise as the powder loading is increased from 10 to 15 kg and finally to 20 kg.

As clearly shown in Figure 46 these foams possess a more open cellular structure characteristic of foams produced with the use of blowing agents. The foams were cut to remove the edges and integral skins from top and bottom to show the size effect due to the increased powder loading and the rather poor cellular structure on the outer periphery of the foam.

Foaming to a shaped configuration in a mold accomplished the objective of reducing the foam collapse during curing. This is shown in Figure 47 where the two foams are produced from the same powder precursor and at the same foaming conditions. The foam shown in Figure 47(a), produced by free-rise technique, shows a denser cellular structure at the base of the bun due to foam collapse. In contrast, the foam shown in Figure 47(b) produced by mold

Figure 46. 1720-1 Foams Produced in a Mold at Various Loadings
132M - 10 kg, 133M - 15 kg, 135M - 20 kg

foaming technique, possesses higher foam rise and no signs of collapse. The principal advantages of foaming to a configuration in the open mold, as reported in Table 20, are:

- more regularly shaped buns
- less foam collapse
- higher rough cut yield
- more homogeneous cellular distribution
- more uniform physical properties within the buns
- more consistent physical properties between buns

Another mold having dimensions of 101.6 cm x 121.9 cm x 91.4 cm (40 x 48 x 36 in.) deep was fabricated as shown in Figure 48. This mold has an open lattice structure which, when fitted with foam liners was expected to allow the volatiles to escape more readily. This mold was evaluated to study the effect of the open lattice structure on foaming behavior of 1720-1 precursors. The foams produced in this mold possessed more imperfections and lower rise than those made in the conventional open box mold used in the development studies

Figure 47(a). Polyimide Foam Produced by Free-Rise Technique

Figure 47(b). Polyimide Foam Produced by Constrained Technique

Table 20

Free Rise Versus Constrained Rise; Effect on Yield and Foam Properties

	FREE RISE	MOLD
Foam No.	150	168M
Powder Resin	1720-1	1720-1
Spray Dryer Outlet Temp. °C	56-60	56-60
AS-2 Conc., %	1.0	1.0
Powder Coating Size, in. cms	15 x 20 x 4.75 38.1 x 50.8 x 12.1	20 x 21 x 4.25 50.8 x 53.3 x 10.8
Powder Load, kg lbs kW/kg	10 22 0.84	10 22 0.84
Bun Size, after Foaming, in. cms	35 x 40 x 19 88.9 x 101.6 x 48.3	32 x 32 x 26 81.3 x 81.3 x 66.0
Bun Size, after Curing, in. cms	35 x 40 x 11.5 88.9 x 101.6 x 29.2	32 x 32 x 24 81.3 x 81.3 x 61.0
Rough Cut Yield, BF	112	171
Foam Characteristics	Homogeneous cellular structure; denser at bottom due to collpase	Homogeneous and uniform cellular structure; some flaws and imperfections at the bottom and outer periphery
Collapse, %	39.5	7.7
Density, lbs/ft^3	0.88	0.83
Compression Set, 90% 50%	37.2 11.4	42.7 14.0
ILD, lbf 25% 65%	37.5 139.0	32.9 111.0

reported earlier. These results were attributed to the higher heat losses occurring in the open lattice mold during the foaming process.

On the basis of these results, the box mold was selected as the standard tool for the development work planned in the remaining tasks of this program.

4.3.2 Foaming Parameters

The objective of this subtask is the continuing evaluation of foaming and compositional parameters to obtain foams by open mold foaming techniques

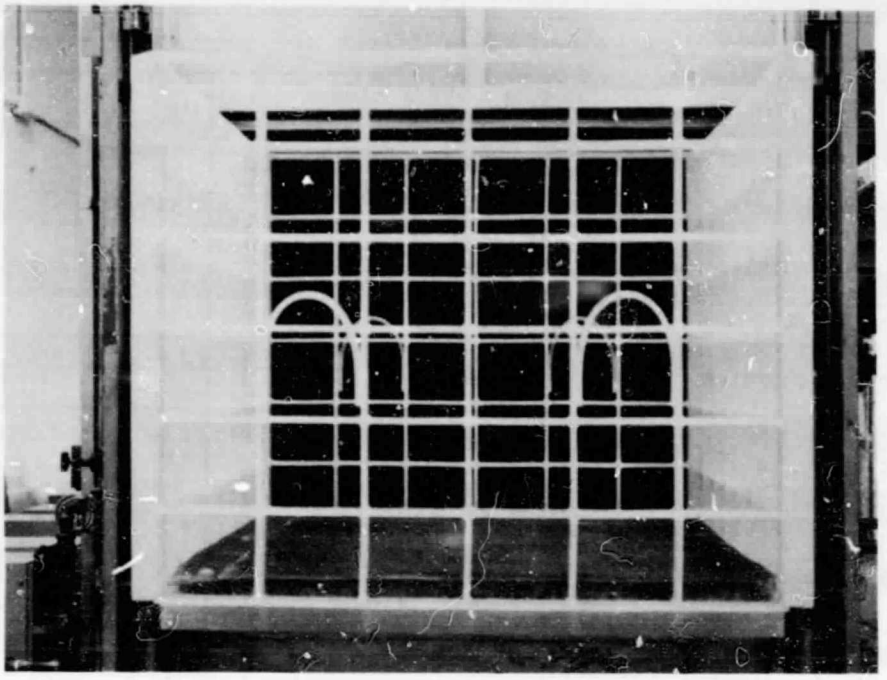


Figure 48. Open Lattice Polyproplene Mold

possessing homogeneous cellular structure and uniform distribution of physical properties within and between buns for classification into five groups of flexible, resilient polyimide foam products in accordance with specified ILD values at 25 percent deflection. All foams in this subtask were tested using the destructive methods described in Task II which permitted sampling the foam from different sections (e.g., top, center, and bottom). All samples were cut perpendicular to the rise of the foam. The testing schematic for foam cut-up and number location was shown in Figure 42.

The foaming and compositional parameters studied in this subtask included the effect of power ratio, concentration of the blowing agent, pulsing cycle and microwave cure times. All foams were extensively tested concurrently with Subtask 4.3.4, Mechanical Testing.

Power Ratio

In the first stage of this study the effects of power ratio on the critical properties of foams were evaluated. All foams in this study were produced from powder precursors spray dried at an outlet temperature of 56-60°C and modified with 2.5 percent blowing agent. Power ratios in the range of 0.3 to 1.7 kW/kg were evaluated. The results of this study are presented in Table 21.

Table 21

Summary of Microwave Power Output Study (kW/kg)

Foam Number	Loading		Power	Power Ratio	Properties				
						Compression Set Loss (%)		ILD, lbf	
	kg	lbs	kW	kW/kg	Density lbs/ft^3	50%	90%	25%	65%
12	15	33	4.5	0.3	1.02	11.9	43.8	28.3	119
10	15	33	6.0	0.4	0.81	16.6	54.5	25.3	86.0
9	15	33	7.5	0.5	0.91	14.1	44.8	35.4	144
8	15	33	9.0	0.6	0.83	17.5	53.3	30.4	93.6
7	15	33	10.5	0.7	0.87	16.4	51.4	32.4	126
6	15	33	12.0	0.8	0.98	11.9	50.1	35.4	144
13	15	33	13.0	0.9	0.94	12.3	38.2	30.4	105
18	14	30.8	14	1.0	0.81	15.6	48.7	27.4	81.0
17	12.72	27.98	14	1.1	0.76	14.4	47.0	27.8	79.1
16	11.66	25.65	14	1.2	0.80	12.7	47.4	28.3	83.5
15	10.8	23.76	14	1.3	0.81	12.4	46.5	32.9	101
14	10.0	22.0	14	1.4	0.87	14.2	45.9	31.3	98.7
19	9.33	20.52	14	1.5	0.78	13.0	44.9	40.5	157
20	8.75	19.25	14	1.6	0.65	13.6	48.9	32.9	121
21	8.235	18.11	14	1.7	0.65	11.8	37.3	26.2	114

The data show that the microwave power ratio does not affect the ILD values of polyimide foams. The most significant contribution of this study was the complete lack of reticulated areas in the foams produced between the range of microwave power ratio of 1.0 to 1.7 kW/kg. This is believed to be the result of the blowing agent used in the powder precursor which decomposed homogeneously at these high power levels and helped to obtain a more uniform distribution of the heat during the expansion process.

Prior to the improvements of polyimide technology by incorporating a blowing agent, reticulation was believed to be a desirable property because it improved the compression set properties. However, it was recognized that reticulation resulted in less durable foams when subjected to cyclic fatigue testing. As the power output study resulted in foams with no reticulation, this evaluation was extended to three specific levels of power ratios, selected to understand the relationship between power output, concentration of blowing agent and critical foam properties. The results of this study are reported in the next section.

Concentration of Blowing Agent

The effect of the concentration of blowing agent at power/°F levels of 1.0, 1.3, and 1.7 kW/kg was discussed in Task II and data presented in Table 7. These foams were produced in the 15 kW GFE microwave oven by molding techniques using powder precursors spray dried at 56-60°C (132.8-140°F) and modified with blowing agent concentrations of 0, 0.25, 0.5, 1.0, 2.5, 5.0 and 7.5 percent. Foams produced in this study are shown in Figure 49 and identified from left to right for increasing power level and from bottom to top for increasing concentration of blowing agent.

Graphical representations of the data presented in Table 7 are shown in Figure 50 for compression set values, Figure 51 for ILD values, and Figure 52 for density.

At each power ratio level (1.0, 1.3, and 1.7 kW/kg), the ILD values of the foams generally decrease with increasing concentration of the blowing agent. The compression set values of the foams improve at blowing agent concentrations of 0.5 percent and higher. The density of the foams generally decreases with increasing concentration of the blowing agent. In all cases, the foams produced at 1.3 kW/kg appeared to have the most uniform cellular structure and distribution of properties within and between buns. At this power level, local overheating during foaming or collapse during curing was essentially eliminated.

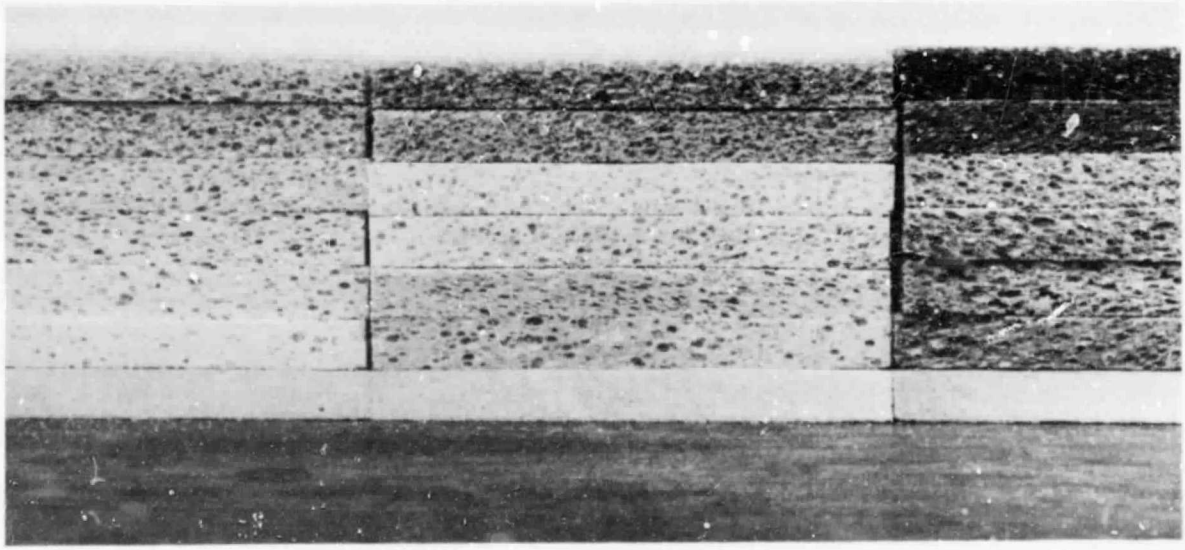


Figure 49. Effects of Power Ratio and Concentration of Blowing Agent at 0, 0.25, 0.50, 1.0, 2.5, 5.0, 7.5 Percent at 1.0, 1.3, 1.7 kW/kg

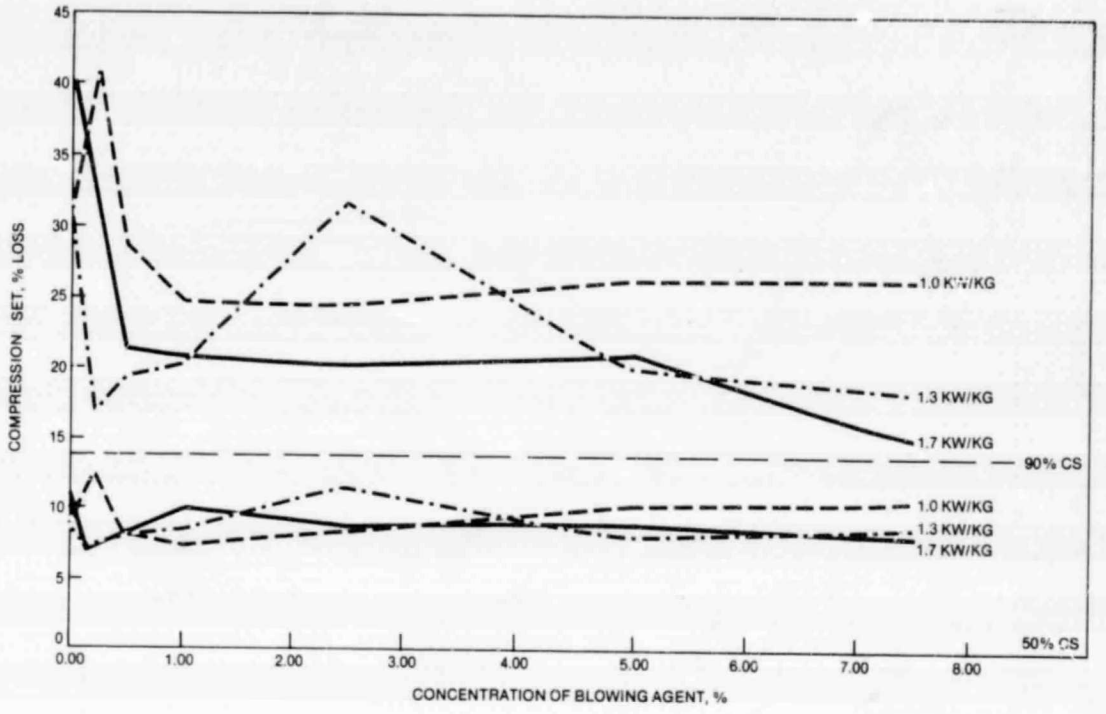


Figure 50. Effect of Power Ratio and Concentration of Blowing Agent on Compression Set Loss of Polyimide Foams

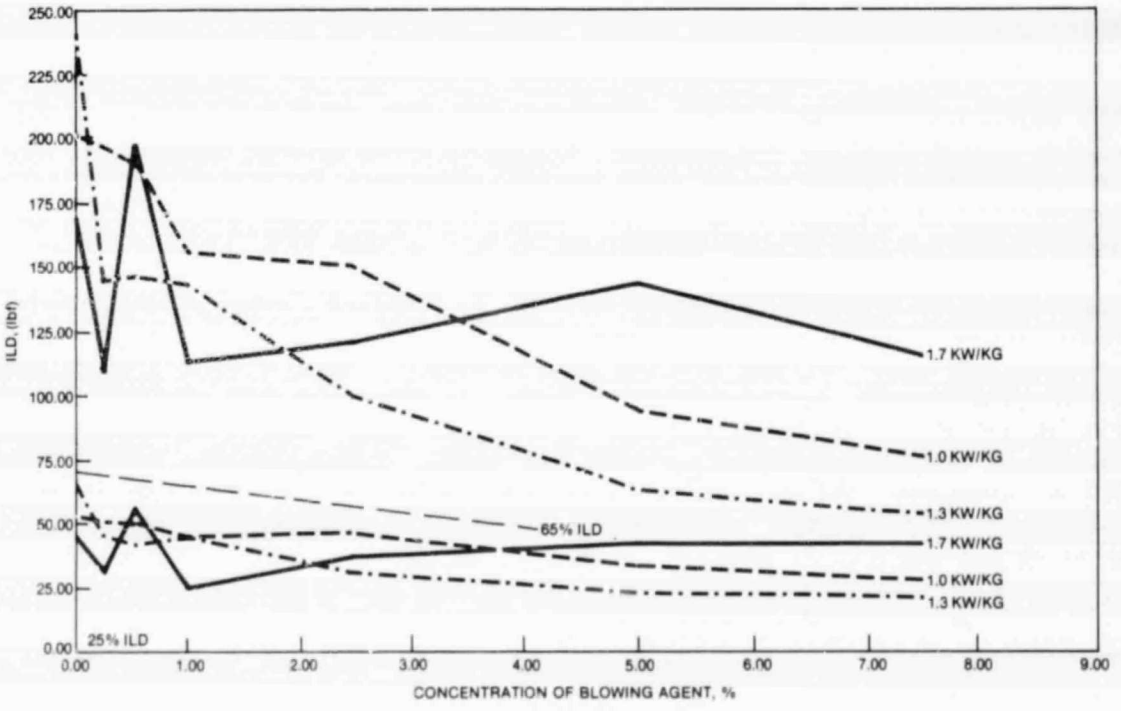


Figure 51. Effect of Power Ratio and Concentration of Blowing Agent on ILD Values of Polyimide Foams

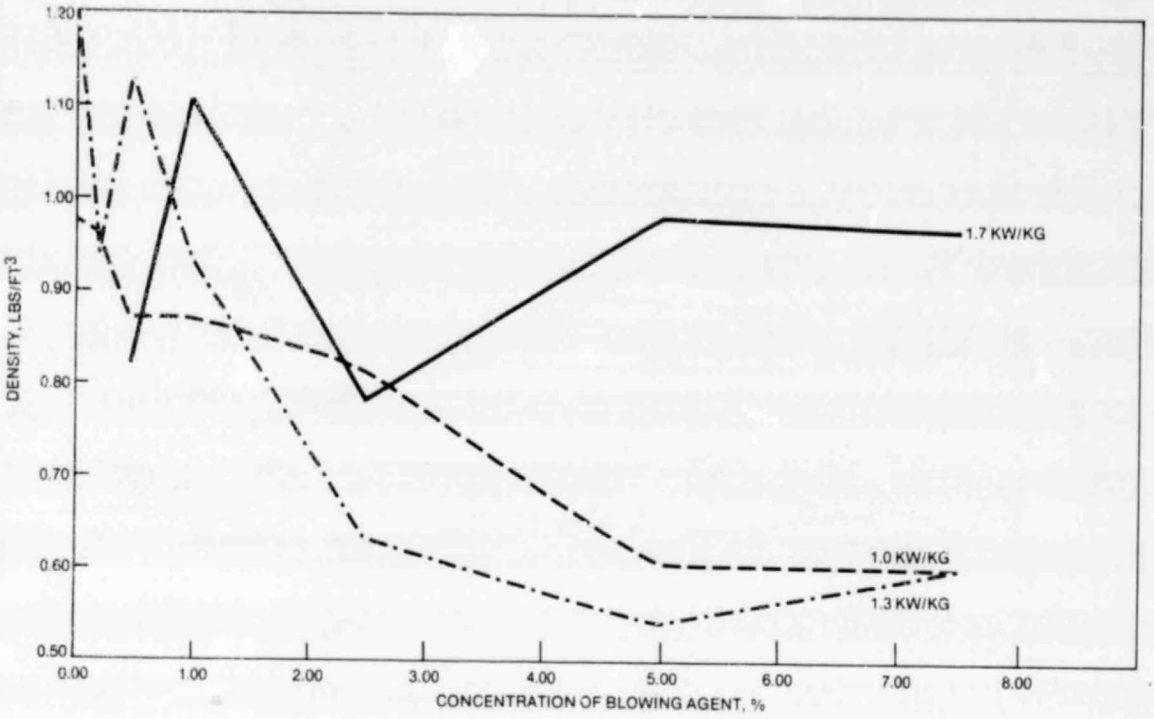


Figure 52. Effect of Power Ratio and Concentration of Blowing Agent on Density of Polyimide Foams

Pulsing Cycles

The objective of this section involved the evaluation of microwave pulsing cycles during foaming and curing. All foams were produced in the 15 kW GFE microwave oven at 1.3 kW/kg from powder precursors spray dried at an outlet temperature of 56-60°C (132.8-140°F) and modified with 2.5 percent blowing agent. The results of this study are shown in Table 22.

Data show that pulsing cycles do not affect the ILD values of the foams and have little effect on the compression set properties. Foams produced at a constant OFF time of 20 seconds and increasing length of ON time show a wider scatter of compression set values. As the length of ON time increased the amount of reticulation and number of flaws increased. This was especially evidenced by the poor quality of foams produced at ON times of 60 seconds and 80 seconds. The optimum pulsing conditions were found to be 20 seconds ON and 20 seconds OFF. This was adapted as a standard pulsing cycle and used in all subsequent work.

Microwave Curing

This study was carried out at three specific microwave power ratios using the following microwave curing time ranges of: 40-60 minutes at a power ratio of

Table 22

Effect of Microwave Pulsing on Properties of Polyimide Foams

Foam Number	142					140					137					138					145				
Pulsing	5/5					20/20					40/20					60/20					80/20				
	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D
	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)
1	27.3	100	17.3	57.4	0.63	33.1	102.7	11.0	38.3	0.65	27.8	88.6	7.5	32.9	0.73	22.8	70.8	8.4	35.9	0.59	32.6	103.7	8.3	37.2	0.77
2	24.8	88.6	14.7	61.2	0.66	30.9	101.2	11.8	57.6	0.70	29.4	88.8	10.4	46.7	0.61	22.3	70.8	11.5	45.3	0.57	24.0	73.4	11.2	44.0	0.67
3	38	129.0	15.1	46.6	0.69	42.3	129.0	10.5	32.9	0.79	37.4	110.6	6.9	23.8	0.74	35.4	110.1	9.5	35.8	0.67	44.3	130.3	11.0	34.9	0.82
4	28.0	97.2	12.8	58.5	0.66	30.4	94.9	14.3	47.8	0.66	29.1	96.1	9.9	41.4	0.61	31.1	106.3	11.8	56.9	0.64	32.6	106.3	11.1	43.6	0.72
5	27.6	93.6	13.1	53.6	0.66	43.5	134.6	11.4	37.6	0.77	40	122	10.8	49.2	0.72	3[illegible].9	112.6	11.8	48.4	0.63	40.7	130.3	14.7	52.9	0.76
6	31.1	107.5	13.4	51.8	0.68	33.4	107.5	11.2	38.6	0.66	34.9	111.3	9.3	48.1	0.67	27.1	91.1	8.4	46.2	0.62	32.4	103.7	12.0	47.6	0.76
7	26.6	92.4	14.8	59.0	0.65	28.0	87.3	10.0	32.5	0.67	24.8	77.9	8.3	34.7	0.61	27.3	89.8	10.4	46.8	0.60	26.3	82.2	10.4	45.9	0.63
8	36.2	140.4	16.4	52.5	0.76	39.5	136.6	10.5	38.2	0.[illegible]	32.9	112.6	6.5	24.5	0.83	34.4	120.2	9.0	37.5	0.75	29.6	106.3	9.0	36.3	0.80
9	29.4	112.6	19.2	56.8	0.70	29.9	111.3	14.9	50.9	[illegible]	21.4	77.4	7.5	31.1	0.58	26.[illegible]	98.7	11.6	52.[illegible]	0.[illegible]	25.8	98.7	9.7	46.5	0.74
Foam Number	135					136					143					144					141				
Pulsing	3/3					10/10					15/15					30/30					40/40				
	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D	ILD (lbf)		CS (%)		D
	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)	25	65	[illegible]	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)	25	65	50	90	(lbs/ft^3)
1	29.3	96.1	14.1	54.8	0.60	23.3	78.9	10.7	51.0	0.55	29.6	103.7	13	44.7	0.65	37.9	129.0	14.0	51.5	0.73	41.2	132.6	14.7	48.9	0.70
2	28.3	89.8	13.7	65.1	0.59	23.3	79.1	13.9	60.9	0.62	29.1	105.5	16.6	60.9	0.68	28.8	93.6	12.6	62.4	0.68	25.3	83.5	[illegible]	[illegible]	0.63
3	34.2	125.2	12.9	44.2	0.71	34.2	107.5	10.7	36.5	0.62	39.7	132.8	13.9	37.4	0.73	46.0	151.8	11.3	38.7	0.81	48.1	[illegible]46.7	[illegible]	34.9	0.76
4	28.1	102.5	14.2	59.9	0.67	29.0	101.2	14.8	52.0	0.63	34.4	118.9	14.8	51.5	0.68	34.2	116.4	14.6	45.0	0.73	35.7	115.6	15.0	[illegible]2.6	0.66
5	31.9	111.3	14.5	50.4	0.69	29.7	101.2	11.7	48.0	0.63	38.2	129.0	12.9	40.8	0.72	28.8	92.3	12.2	43.9	0.68	36.4	113.9	[illegible]	43.6	0.68
6	31.1	102.5	14.3	55.9	0.65	25.1	87.7	13.7	47.8	0.60	30.4	103.7	14.0	50.0	0.70	36.9	129.0	13.8	41.4	0.70	30.1	96.1	12.9	43.6	0.65
7	23.3	82.2	12.6	56.7	0.64	25.6	87.5	19.2	39.9	0.61	29.9	101.2	12.1	43.1	0.69	29.8	97.4	11.2	39.9	0.69	38.7	124	10.0	39.3	0.[illegible]
8	31.4	116.4	14.8	55.3	0.69	32.1	113.9	10.8	43.9	0.73	41.5	151.8	13.0	45.4	0.80	42.2	153.1	10.7	37.2	0.84	41.5	139.2	10.7	35.2	0.85
9	25.1	96.1	13.9	61.4	0.64	27.6	106.3	11.7	48.1	0.67	26.6	101.2	17.7	55.8	0.68	26.6	101.2	12.3	38.8	0.70	30.9	117.1	14.8	45.4	0.74

1.0 kW/kg, 35-55 minutes at 1.3 kW/kg, and 25-45 minutes at 1.7 kW/kg. These foams were produced from 1720-1 powder precursors spray dried at an outlet temperature of 56-60°C (132.8-140°F) and modified with 2.5 percent blowing agent. In all cases the foams were produced in the 15 kW GFE microwave oven at the selected microwave power ratio, and microwave cured at 14.0 kW for a specified length of time. The foams were then thermally post-cured at 350-475°F (176.6-246.0°C) for a period of one hour and 35 minutes. The results of this study are shown in Tables 23, 24 and 25 for power ratios of 1.0, 1.3 and 1.7 kW/kg, respectively.

Figure 53 through Figure 58 are graphical representations of data obtained from this study which are briefly discussed below.

The data show that the ILD properties within the foam do not vary with changes of the microwave curing time within the range reported. The ILD values are generally homogeneous with the exception of the bottom section which shows higher values due to slight foam collapse.

The compression set properties within the foam are dependent on power ratio and curing time and are best in the center section of the foam. The most homogeneous compression set values were obtained at a power ratio of 1.3 kW/kg and microwave curing time of 40-45 minutes. At this ratio the values of the 90 percent compression set within the foam vary between a low of 21 and a high of 47.7.

Additional work was subsequently carried out to better define the microwave curing time. Foams were produced at a microwave curing time of 40, 41, 41.5, 42.0, and 42.5 minutes. Results indicated that the most homogeneous distribution of critical properties is obtained at a microwave curing time of 42.0 minutes using a foaming power ratio of 1.3 kW/kg.

4.3.3 Optimization of the Comfort Index of Polyimide Foams

Comfort index, which is an extension of ILD test, is defined as the ratio of ILD at 65 to 25 percent deflection. The value of this ratio is a measure of the seating comfort of the foam and should be in the range of 2.0 to 6.0 to cover the properties of foams for all five classes.

The prime requirement of a cushion is a combination of low compression set, good recovery and high resiliency. To obtain these properties, the foams must be free of closed cells. To determine the closed cell content of the foams an Air Pycnometer (Beckman Model 930; Fig. 59) was obtained and used to determine the effectiveness of the various methods in increasing the open cell content using the procedure described in ASTM D2856-30. Table 26 lists the open cell content of two foams before and after processing and clearly indicates that polyimide foams produced by microwave process have an open cell structure, therefore they do not require processing to improve this property. What processing has done to polyimide foams is to decrease the rigidity of the foams which we had believed was caused by the rupture of the closed cell of the foams.

Table 23

Effect of Microwave Curing Time on Properties of Polyimide Foams

1.0 kW/kg Foaming = 8.2 kW Curing = 14.0 kW

Foam #	116					117					118					119					120				
Curing Time (Min.)	40					45					50					55					60				
Sample Location	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C S.		D
	25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%	
1	34.8	118.9	16.6	52.7	0.68	33.4	116.9	15.8	57.1	0.66	36.4	113.9	14.8	47.5	0.74	37.7	129.8	10.4	47.2	0.90	34.16	109.3	9.7	27.6	0.87
2	36.3	133.8	20.1	61.5	0.71	37.5	129.5	17.8	62.4	0.80	32.9	118.2	13.3	54.3	0.77	44.8	150.3	11.9	51.5	0.88	38.2	110.6	14.3	59.5	0.03
3	34.8	117.1	14.7	40.3	0.82	41.0	136.6	13.5	31.5	0.80	37.7	113.9	9.4	20.2	0.76	39.2	118.9	7.5	18.9	0.73	9.5	36.5	8.1	15.9	0.70
4	22.5	80.5	12.7	31.9	0.68	34.9	118.9	16.9	51.1	0.75	29.1	86.0	9.6	30.5	0.70	30.6	92.4	7.9	28.4	0.68	27.9	98.2	9.7	20.4	0.77
5	28.0	112.3	17.4	48.7	0.77	29.2	97.6	10.1	39.5	0.67	37.2	117.7	12.6	35.9	0.77	34.4	106.8	9.1	26.8	0.78	35.4	121.4	8.8	18.0	0.82
6	26.6	94.1	18.9	48.5	0.74	27.8	96.1	10.1	23.7	0.66	39.7	129.8	10.7	35.5	0.79	25.8	83.0	10.6	24.6	0.72	20.5	72.2	9.8	26.3	0.74
7	23.9	88.6	14.8	58.3	0.73	25.0	86.3	13.2	38.1	0.63	36.9	122.7	12.6	37.7	0.78	30.5	93.6	7.9	23.3	0.67	34.4	105.5	9.5	19.2	0.73
8	38.4	149.8	15.6	44.9	0.80	52.1	187.7	11.7	32.1	0.90	51.1	180.9	8.4	18.9	1.04	59.7	223.2	7.7	19.4	1.38	36.5	139.2	7.0	13.7	1.10
9	35.3	148.5	16.4	48.6	0.87	33.?	144.2	14.4	51.5	0.83	35.4	130.3	11.8	42.1	0.83	39.5	140.4	15.6	50.1	0.82	46.1	174.6	12.7	24.2	0.99

Table 24

Effect of Microwave Curing Time on Properties of Polyimide Foams
1.3 kW/kg Foaming = 10.7 kW Curing = 14 kW

Foam #	121					122					123					124					125				
Curing Time (Min.)	35					40					45					50					55				
	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D
Sample Location	25%	65%	50%	90%	lbs/ft^3	25%	65%	50%	90%	lbs/ft^3	25%	65%	50%	90%	lbs/ft^3	25%	65%	50%	90%	lbs/ft^3	25%	65%	50%	90%	lbs/ft^3
1	35.4	120.2	13.9	44.6	0.65	35.2	107.5	13.6	50.2	0.66	31.4	98.2	10.0	30.5	0.66	47.6	149.3	7.1	26.4	1.19	16.1	65.4	5.1	15.0	0.64
2	28.8	98.7	10.6	47.6	0.63	30.8	98.2	13.6	52.3	0.62	30.9	103.7	13.3	47.7	0.64	32.9	117.7	9.4	52.0	0.79	14.2	44.0	7.5	23.0	0.58
3	39.0	130.0	11.0	31.4	0.71	48.4	144.2	11.3	34.4	0.74	28.3	83.5	6.4	21.0	0.61	49.6	141.7	7.0	22.0	0.97	7.6	40.2	2.5	7.3	0.52
4	35.4	120.2	13.7	44.2	0.67	31.1	100.0	11.6	32.0	0.61	32.1	100.4	13.4	41.9	0.65	44.8	144.2	10.7	34.2	0.99	16.2	53.9	5.[illegible]	18.0	0.62
5	29.9	98.7	11.0	35.6	0.64	30.3	94.6	10.5	33.1	0.64	29.0	86.0	9.7	32.6	0.63	31.8	105.0	8.1	25.0	0.85	17.6	56.7	5.8	15.4	0.57
6	35.2	120.2	11.8	35.6	0.67	32.6	105.3	10.9	37.3	0.70	28.1	88.3	12.3	34.0	0.64	31.4	96.7	9.9	39.0	0.71	20.6	61.0	6.7	17.2	0.78
7	31.3	103.7	12.9	35.4	0.65	25.3	76.1	9.6	32.5	0.62	25.8	78.4	8.8	35.5	0.64	28.1	86.5	7.5	22.0	0.81	11.1	41.6	5.0	18.3	0.56
8	34.6	134.9	11.8	37.4	0.75	51.3	164.5	9.4	30.9	0.98	42.7	132.3	7.3	22.3	0.91	47.3	167.0	6.7	23.8	1.16	27.1	106.3	2.9	6.8	1.03
9	29.9	121.5	11.7	37.2	0.70	32.4	115.1	10.8	42.0	0.70	29.3	85.5	12.5	29.5	0.70	39.0	146.7	8.7	37.7	0.89	24.8	78.9	8.4	21.0	0.68

Table 25

Effect of Microwave Curing Time on Properties of Polyimide Foams
1.7 kW/kg Foaming = 14 kW Curing = 14 kW

Foam #	126					127					128					129					130				
Curing Time (Min.)	25					30					35					40					45				
Sample Location	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D	ILD		C.S.		D
	25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%		25%	65%	50%	90%	
1	28.8	93.6	14.8	51.3	0.57	36.7	112.8	13.0	39.7	0.64	28.8	94.9	8.1	34.3	0.83	41.6	136.1	8.2	29.6	0.90	38.7	118.9	7.8	25.1	0.86
2	29.8	95.[illegible]	14.7	54.9	0.58	26.6	86.0	13.5	54.9	0.58	27.6	86.5	12.2	47.4	0.68	31.6	98.7	11.8	43.3	0.67	22.3	75.4	11.3	36.7	0.63
3	34.8	115.6	16.1	56.6	0.64	49.6	151.8	10.5	31.3	0.73	44.2	133.3	7.1	22.8	0.85	37.2	118.4	6.8	16.9	0.77	31.9	107.0	7.8	20.9	0.84
4	31.6	108.3	14.6	55.7	0.62	30.1	100.4	13.3	52.7	0.60	26.6	84.8	11.6	39.3	0.71	33.9	107.0	12.8	32.6	0.77	34.4	116.9	8.5	31.2	0.80
5	34.0	119.4	15.5	63.0	0.63	35.4	113.1	12.5	40.3	0.65	38.2	117.7	10.9	35.2	0.75	35.4	112.6	9.6	33.0	0.79	21.8	71.8	6.5	21.5	0.72
6	29.3	98.7	13.3	58.2	0.60	35.9	117.6	13.9	45.1	0.76	31.5	102.5	10.9	31.1	0.72	29.6	95.4	10.0	23.6	0.69	29.5	103.7	8.1	25.4	0.77
7	21.5	70.8	11.5	44.1	0.55	28.4	96.1	11.4	38.1	0.62	24.5	77.7	10.9	28.7	0.65	29.8	76.9	8.6	25.1	0.66	31.1	126.5	7.9	30.8	1.15
8	27.0	96.4	12.7	58.5	0.64	41.5	146.2	10.9	35.8	0.82	50.6	186.5	7.6	28.7	1.13	50.6	210.0	7.6	22.6	1.26	45.5	175.6	8.0	21.4	1.43
9	31.1	118.9	13.6	59.5	0.63	26.6	120.7	12.8	54.0	0.63	24.4	88.6	10.4	46.5	0.66	26.3	96.1	9.6	16.5	0.68	40.2	196.8	10.3	28.9	1.30

C-2

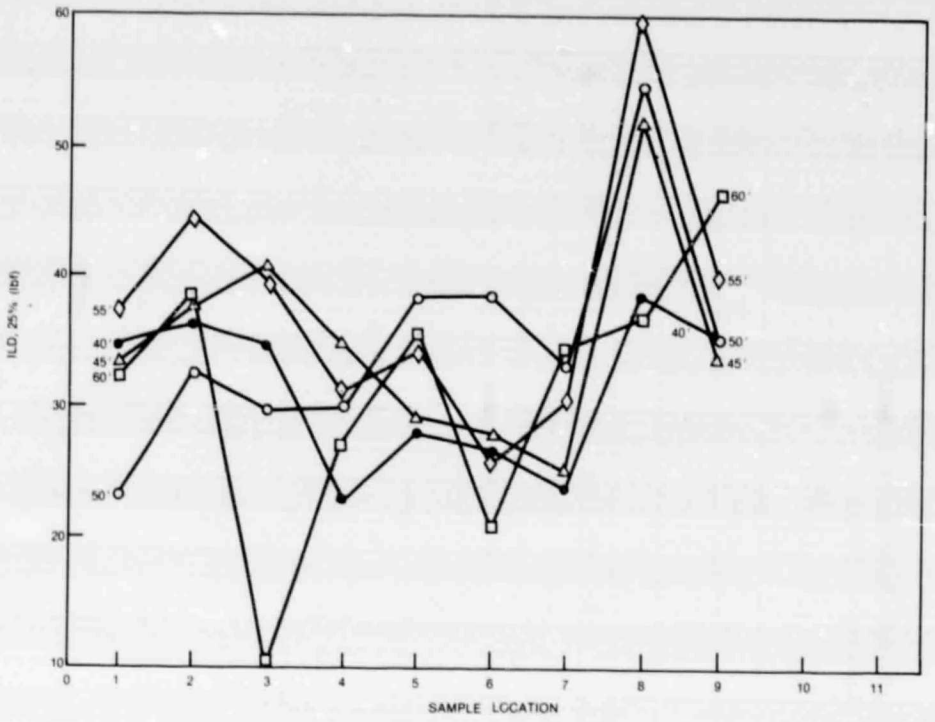


Figure 53. Effect of Microwave Curing Time at a Power Ratio of 1.0 kW/kg on Within Bun Variability of ILD Values of Polyimide Foams

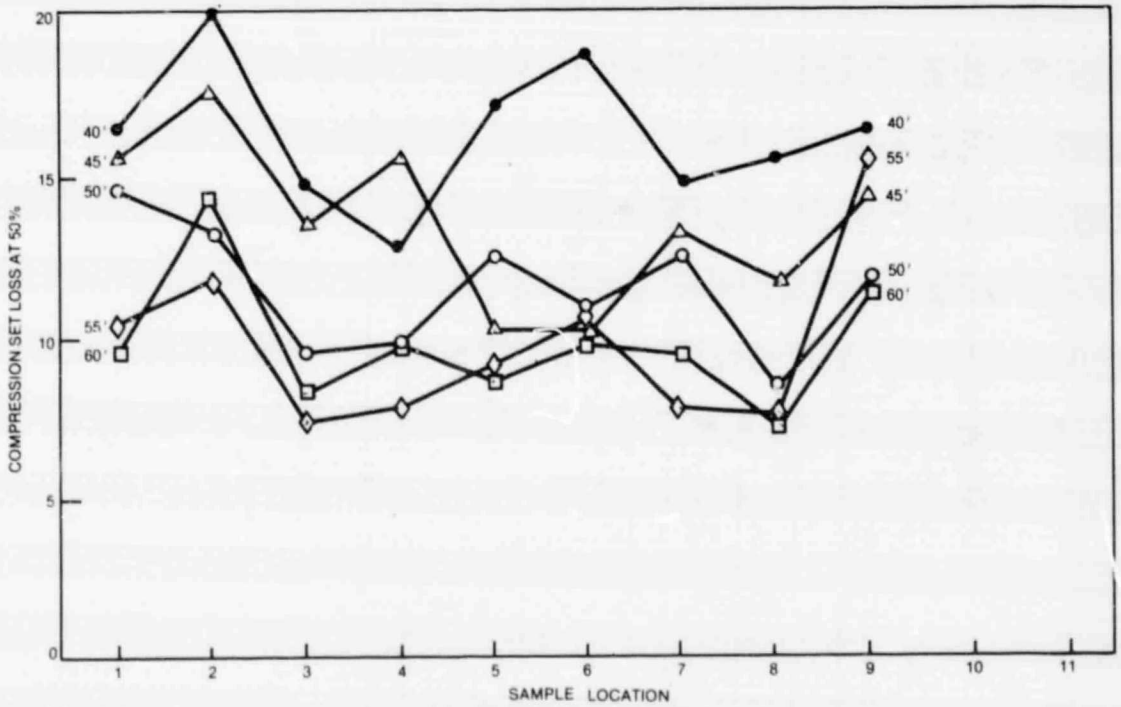


Figure 54. Effect of Microwave Curing Time at a Power Ratio of 1.0 kW/kg on Within Bun Variability of Compression Set Loss of Polyimide Foams

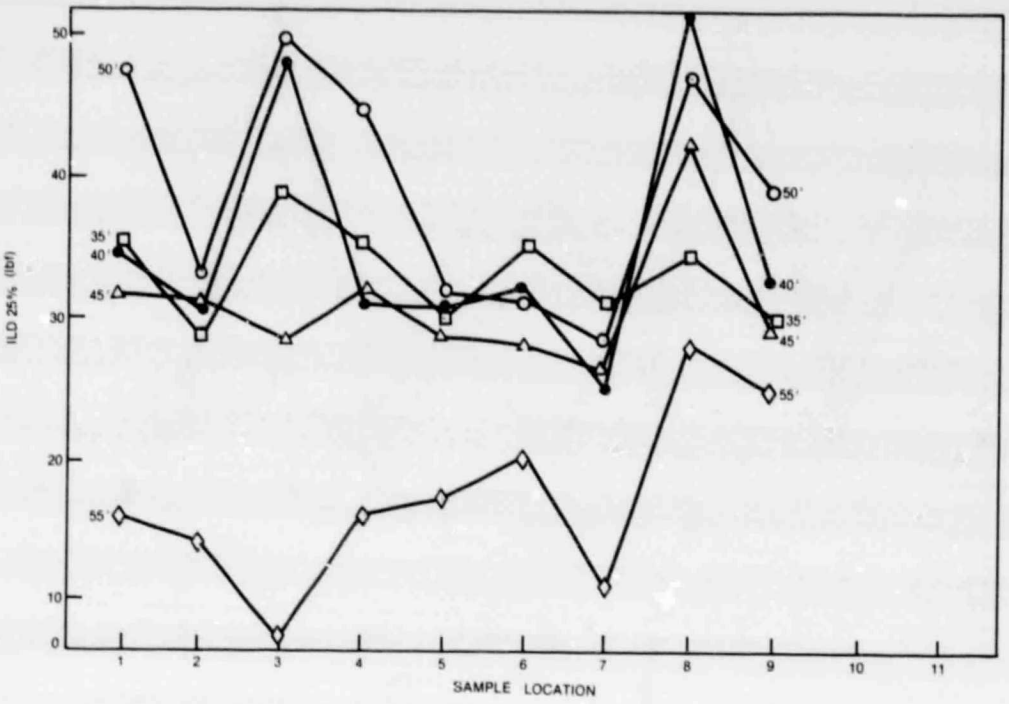


Figure 55. Effect of Microwave Curing Time at a Power Ratio of 1.3 kW/kg on Within Bun Variability of ILD Values of Polyimide Foams

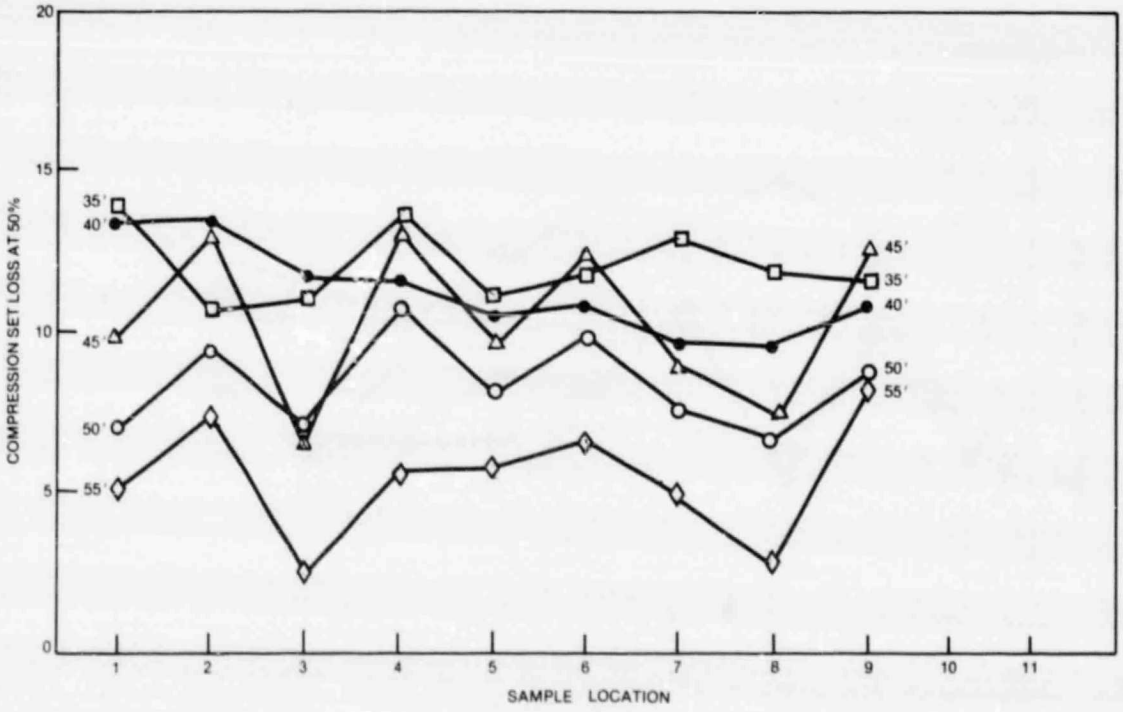


Figure 56. Effect of Microwave Curing Time at a Power Ratio of 1.3 kW/kg on Within Bun Variability of Compression Set Loss of Polyimide Foams

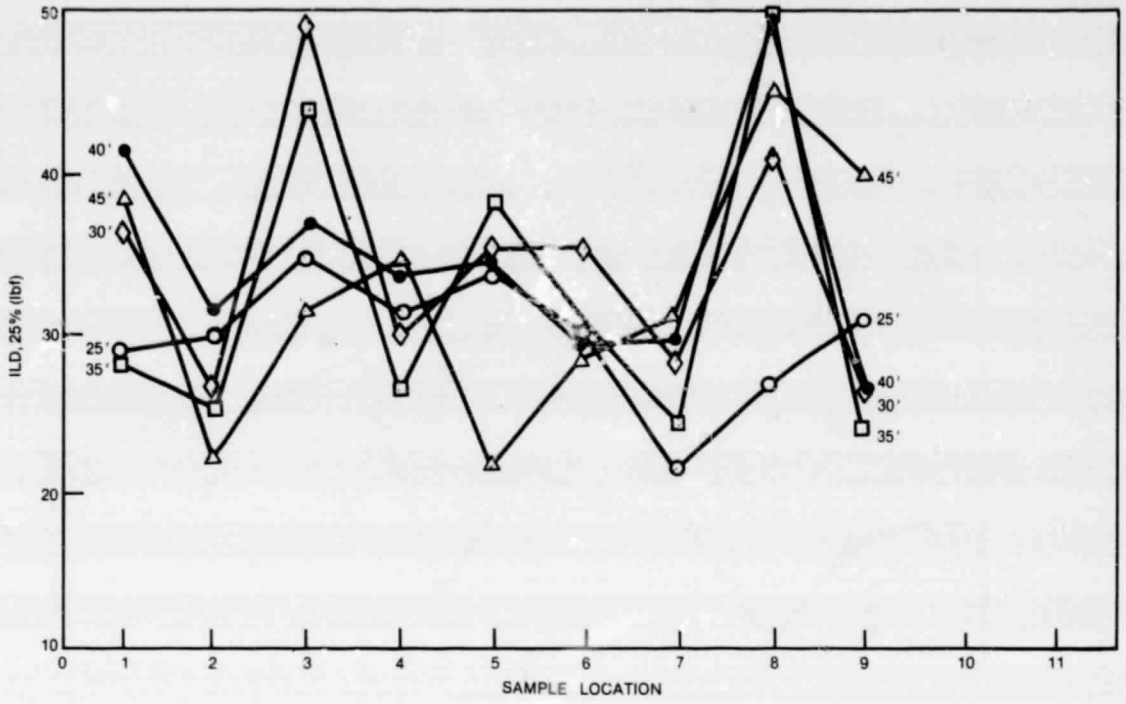


Figure 57. Effect of Microwave Curing Time at a Power Ratio of 1.7 kW/kg on Within Bun Variability of ILD Values of Polyimide Foams

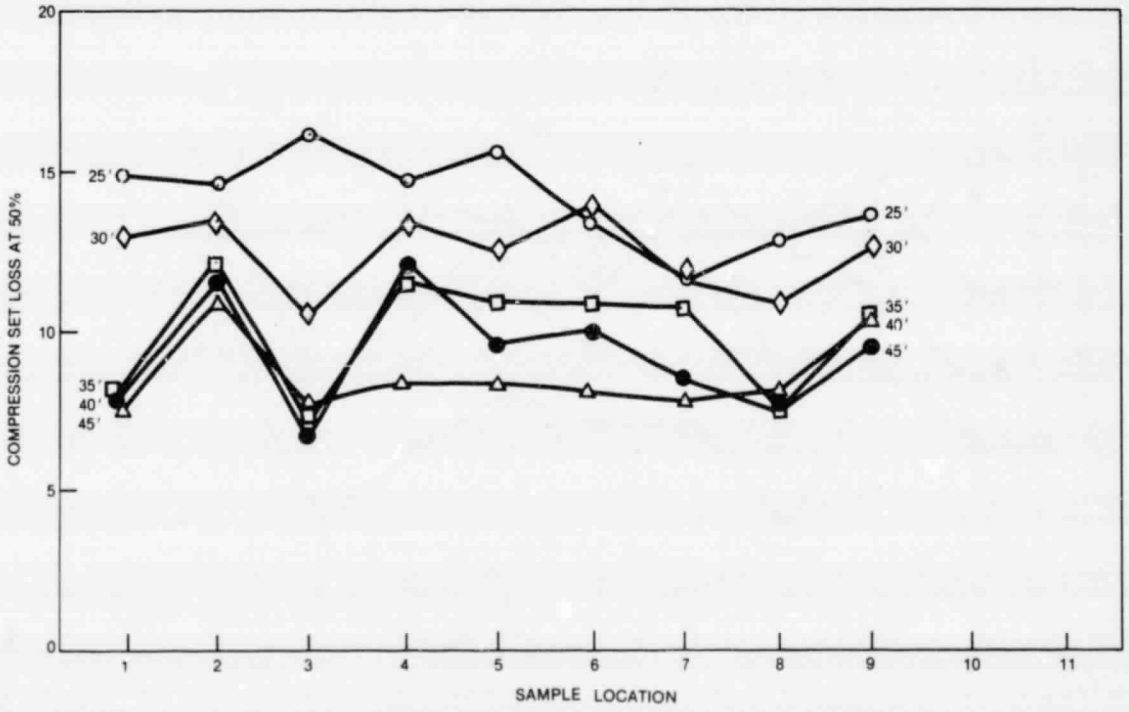


Figure 58. Effect of Microwave Curing Time at a Power Ratio of 1.7 kW/kg on Within Bun Variability of Compression Set Loss of Polyimde Foams

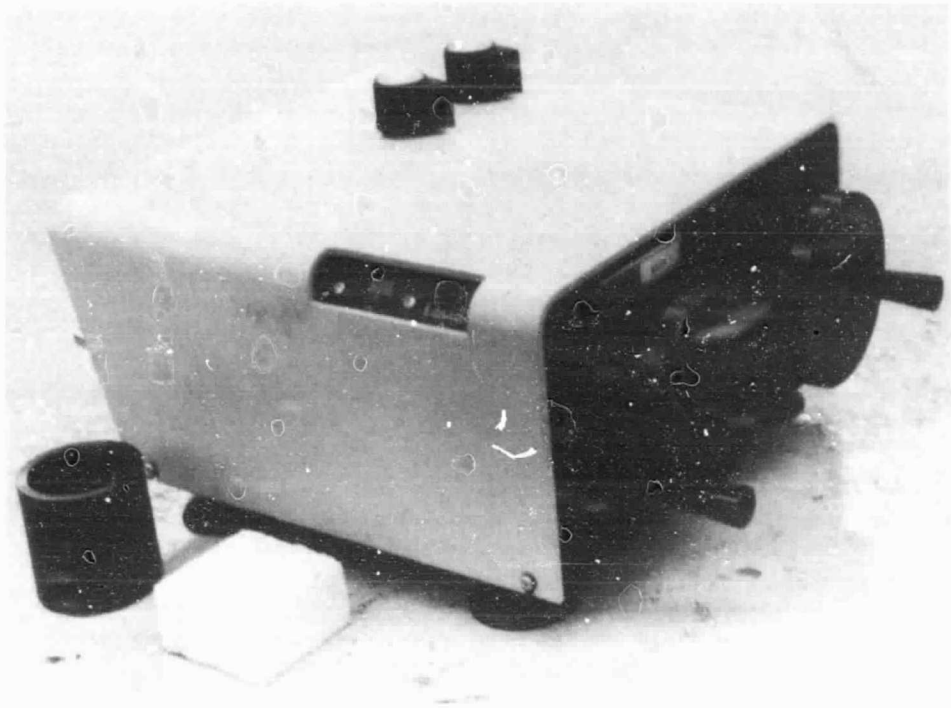


Figure 59. Beckman Model 930 Air Pycnometer

Table 20

Evaluation of Open Cell Content of Polyimide Foams

Open Cell Content of Polyimide Foams (%)		
As Foamed	After Processing	Change (%)
96.5	97.4	<1.0
97.0	97.0	0

Polyimide foam cell walls apper to be composed of two different structures. The structures are: (1) An interconnective network between cells much like the framework of a house and, (2) A thinner structure between the framework similar to the walls in a house, called the cell lamellae. This lamellae structure is generally discontinuous resulting in the high open cell content, but is stiff enough to cause the rigidity apparent in polyimide foams. It is this lamellae structure which must be broken down to increase the softness of the foam, thus lowering the comfort index. A review of the methods used to alter the cellular structure is presented below.

Attempts to reduce the rigidity of polyimide foams by compositional changes of the precursors have resulted in limited success. Chemical methods to achieve the same results have been discussed in Task II under the subtask

dealing with blowing agents. In this last method, the evolution of gas was expected to form a more open cellular structure, thus reducing the lamellae content.

Although significant improvements were achieved, the lamellae content of the polyimide foams produced with blowing agents was still high as evidenced by the high rigidity of the freshly prepared buns. Mechanical methods were then evaluated to lower the foam rigidity in order to upgrade the seating comfort of the polyimide foams. The methods used were needle punching and crushing.

Needle Punching Techniques

This method has been used in the industry to process plastic foam materials although its use is limited to few applications. The method is carried out by punching the foams with sharp pointed needles to rupture the closed cell content and increase the communication between cells.

With the method used in this task the terpolyimide foams were first flexibilized and then processed with a tool fabricated with 0.2286 cm (0.090 in.) diameter needles. Three such tools were fabricated with a needle spacing of 2.54, 1.27 and 0.635 cm (1, 0.5 and 0.25 in.) respectively on a wooden board. The increased needle density was used to evaluate the effectiveness of the process.

The effect of needle punching on the ILD, compression set and comfort index values of terpolyimide foams is shown in Table 27. Needle punching lowers the values of the ILD at 25 and 65 percent deflection. This was expected since the more open cellular structure requires less force to compress. Needle punching however degrades the compression set properties of the terpolyimide foams. This effect may be due to damage of the cell connecting network which reduces the ability of the foams to recover.

This method was abandoned due to the adverse effect on compression set and the lack of improvement on comfort index.

Crushing Techniques

During the early development work on polyimide foams it was recognized that polyimide foams achieved optimum resiliency and flexibility after being flexed or compressed. This process was originally carried out in a platen press at room temperature starting with low deflection rates and increasing the deflection to 90 percent of the original foam thickness. During this process the closed cells were expected to be ruptured and a more flexible foam structure was produced.

A more efficient method was developed during the course of this contractual effort by fabricating a flexibilizer which permits processing foam slabs as large as 1.2 x 2.4 m (4 x 8 ft). This foam flexibilizer was shown in Section

Table 27

Effect of Needle Punching on Terpolyimide Foams

NEEDLE DENSITY needle/in^2	ILD				COMPRESSION SET		COMFORT INDEX
	25%		65%		50%	90%	
	lbf	N	lbf	N			
0	48.5	215.7	219.0	974.1	12.5	37.8	4.5
1	34.5	153.4	164.4	731.2	12.9	37.5	4.8
4	33.8	150.3	167.0	742.8	15.0	49.6	4.9
16	28.8	128.1	149.3	664.0	22.0	47.0	5.1

3. It consists of two adjustable steel rolls, 30.0 cm diameter (12 in.) which rotate at constant speed and compress the foam slab as it moves through the rolls. This process has been used to flexibilize all polyimide foams used in cushioning applications including test samples submitted to NASA-JSC.

Using this tool the foam samples were compressed to a specific thickness for a specified number of times. They were then measured for ILD at 25 and 65 percent deflection. The results of this study are listed in Table 28 and the data obtained for 25 percent ILD are graphically presented in Figure 60. Interestingly, the data appears to be divided into two groups having a dividing point between 6 and 8 flexes. This break after 6 flexes illustrates a change in the physical properties of the foam. This abrupt change is evident in all of the properties but is illustrated most dramatically and consistently by the 25 percent ILD values. This change in the physical properties of the foam indicates an irreversible rupture of the cell lamellae. This process does not affect the fatigue properties of the foams as shown in Table 29. Surprisingly the compression set loss of the foams does not increase but improves slightly. This is most likely due to the increased flexibility and softness imparted to the foam during the crushing process. This soft, flexible foam offers less resistance to compression and therefore is damaged less during compression set testing than a foam which has not been crushed. The comfort index of the foam increased slightly and was still within an acceptable range. The increase of the comfort index is caused by a proportionately lower rate of change for the 65 percent ILD value compared to that obtained with the 25 percent ILD value.

These data indicate that the behavior of polyimide foams is much different from that of polyurethane foams than originally expected due principally to the much stiffer behavior at higher deflection values. At the conclusion of this effort crushing techniques were selected to lower the ILD values and improve the flexibility of the polyimide foams. Additional work on this subject was carried out in a subsequent task to further define the seating characteristics of polyimide foams and to derive suitable specifications.

Table 28

Data Summary; Classes I and II by Flexing Processes

Number of Repetitions		4	6	8	12
Physical Property	Percent Compression				
25% ILD (lbf)	75	50.1	51.3	44.7	44.7
	80	41.6	41.6	36.6	36.6
	85	33.9	34.3	30.5	30.0
	90	27.3	25.9	23.3	22.7
65% ILD (lbf)	75	182	188	167	170
	80	158	163	163	143
	85	131	130	115	120
	90	110	109	94	99
Density (pcf)	75	0.88	0.93	0.90	0.92
	80	0.94	0.99	0.96	0.99
	85	1.00	1.06	1.02	1.08
	90	1.13	1.21	1.17	1.26
Thickness (inches)	75	1.88	1.86	1.86	1.84
	80	1.77	1.77	1.75	1.71
	85	1.65	1.63	1.63	1.57
	90	1.47	1.43	1.42	1.34

4.3.4 Particle Size Distribution

The particle size distribution of the powder precursor has been shown to influence the homogeneity within foams, cell size and cellular structure of polyimide foams.

To obtain foams possessing homogeneous cellular structure and uniform distribution of critical properties, it was necessary to obtain powder precursors with a uniform distribution of particle size. Large particles, possessing higher volatile content, were found to produce reticulated areas. Finer particles invariably produced flaws and imperfections. As these facts were known, it became mandatory to control the particle size of powder precursor within a limiting range. This parameter was studied by varying the particle size distribution of the powder precursor in three different ways:

a. spray dryer processing

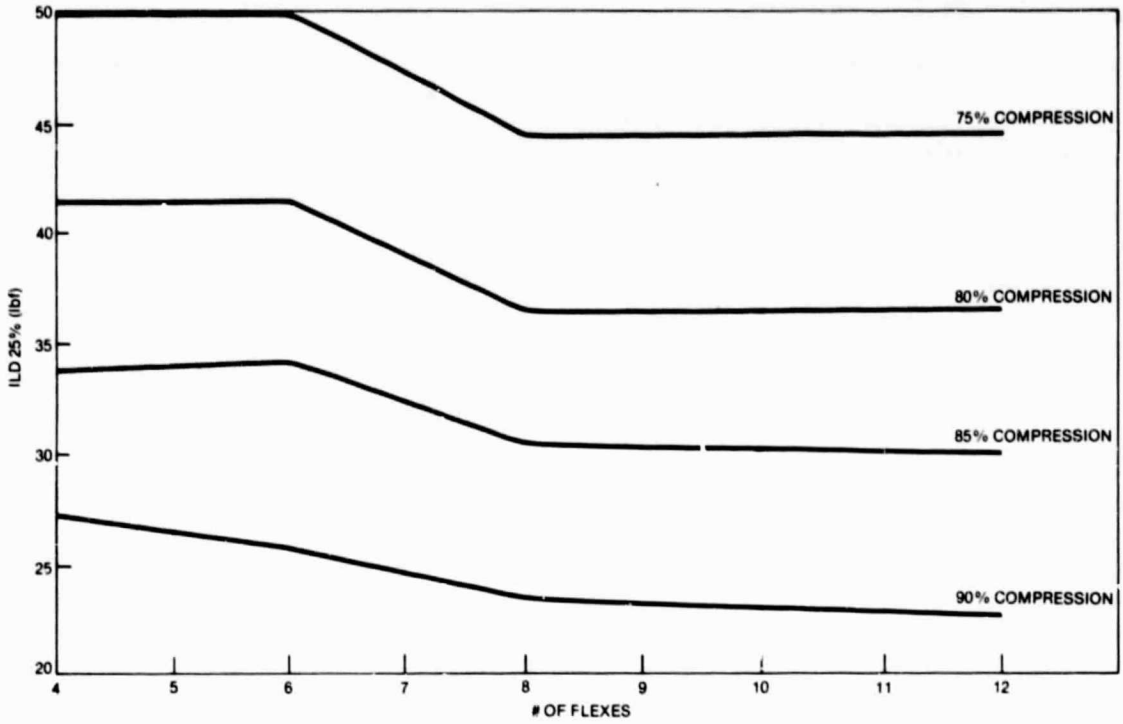


Figure 60. Effect of Crushing on ILD Values of Polyimide Foams

Table 29

Effect of Crushing on Physical Properties of Terpolyimide Foams

Crushing Schedule		Compression[1] Set Loss		Fatigue Loss (%)	ILD				Comfort Index
					25%		65%		
% Comp.	# of Rep.	70%	30%		lbf	N	lbf	N	
75	4	20.1	5.7	4.5	50.1	223	182	810	3.6
80	8	17.7	5.4	11.4	36.6	163	163	725	4.4
90	12	18.6	5.1	9.1	22.7	101	99	441	4.4

[1]Compression set specifications have been modified as discussed in Task III.

b. screening

c. grinding

The effect of the outlet temperature on the particle size distribution of the powder precursors has been discussed previously. The particle size distribution has also been found to be dependent on the spray dryer's atomizer speed. More specifically, the particle size is indirectly proportional to the atomizer speed. This technique has been found to be a valuable tool in obtaining powder precursors with homogeneous particle size distribution from which to obtain foams with specific properties. The other methods used to obtain homogeneous particle size distribution were screening through a sieve and grinding through a Pulvette pulverizer. These methods were less desirable since they produced dust and required recycling.

From the results of these studies the most homogeneous foams were those produced at an atomizer speed of 30,000-35,000 rpm. The powder precursors were sieved through a No. 25 sieve (710 micrometers) to remove any large size chunks. For reproducibility in the sieving operation, a new Vibro-Energy Separator, shown in Figure 61 was installed and used for all foaming operations.

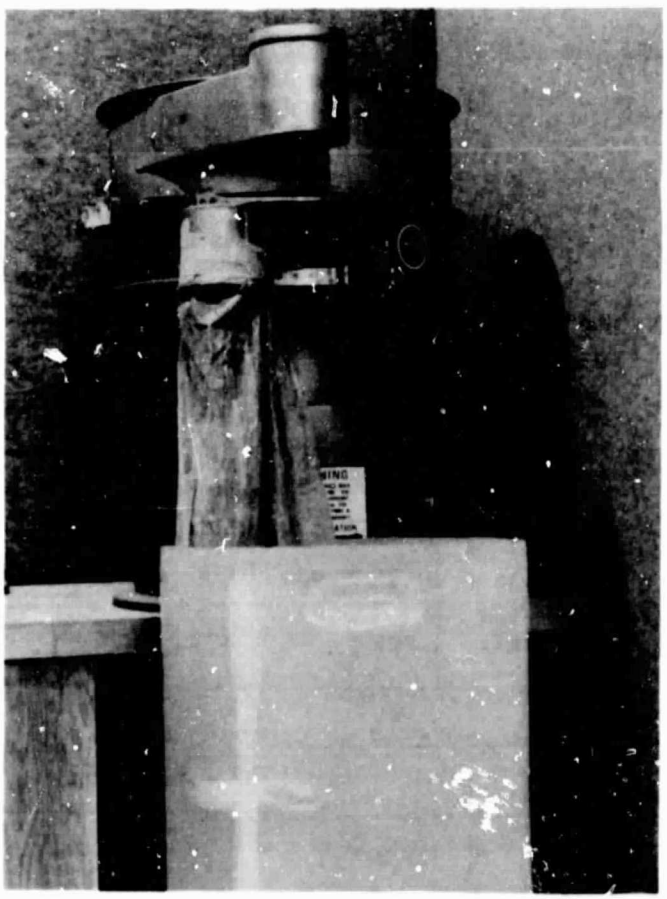


Figure 61.

SWECO Vibro-Energy Separator

4.3.5 Mechanical Testing

The objective of this task is to establish the properties of foams by evaluation of processing parameters and techniques studied or selected through the efforts of preceding sections, and to identify processes which affect the ILD properties of foams. The data obtained in this task were used in subsequent tasks to classify foams according to established ILD values.

In the preceding sections, molding techniques in conjunction with foaming, compositional changes, and processing parameters were discussed. An exhaustive testing program, concurrent with those studies, was carried out to evaluate the effects of these parameters on the critical foam properties. From the data generated, a final foaming process emerged. This process produced polyimide foam products with uniform distribution of properties within and between buns. This optimized process is summarized below.

Powder precursors blended with a specific concentration of blowing agent were foamed in a polypropylene open mold equipped with perforated lid, corner vents, bottom grid and polyimide insulation. The foaming was carried out at a power ratio of 1.3 kW/kg at a constant powder loading of 8.235 kg (18 lbs) and microwave cured for 42 minutes at a power output of 14 kW. A pulsing cycle of 20 seconds ON and 20 seconds OFF was used during the microwave foaming and curing. The foam was then thermally postcured at 350-475°F (176.6-246.0°C) for one hour and 35 minutes.

For test evaluation the foam was cut according to the schematic shown in Figure 42 and the samples tested for critical properties such as density, compression set, ILD, and fatigue resistance. Other properties measured were percent open cell and comfort index.

The efforts of the preceding tasks also resulted in identification of processing and compositional parameters which showed definite relationships with ILD values. These parameters are outlet temperature, concentration of blowing agent, and crushing.

The evaluation of the outlet temperature and concentration of blowing agent was carried out concurrently utilizing the advanced and optimized process reported above. Powder precursors were prepared at four selected outlet temperature ranges and modified with 0.25, 0.5, 1.0 and 2.5 percent blowing agent prior to foaming. These outlet temperature ranges were 59 $\pm$ 1, 64 $\pm$ 1, 69 $\pm$ 1, and 74 $\pm$ 1°C. Results of this study are shown in Table 30 for a temperature of 59 $\pm$ 1°C, Table 31 for a temperature of 64 $\pm$ 1°C, Table 32 for a temperature of 69 $\pm$ 1°C, and Table 33 for a temperature of 74 $\pm$ 1°C (138.2°F, 147.2°F, 156.2°F, 165.2°F, respectively). The data shown in these tables are graphically represented in Figures 62 through 65. For each of the outlet temperature ranges studied, the relationship between the concentration of the blowing agent and the ILD values at 25 percent deflection is shown in Figure 62. Figure 63 shows the effect of blowing agent concentration on the compression set loss at 50 percent, Figure 64 shows the effect on density and Figure 65 on the fatigue resistance.

Table 30

Effect of Concentration of Blowing Agent on Properties of Polyimide Foams at an Outlet Temperature of 59 ± 1°C

Foam Number	210					211					212					213				
Blowing Agent (%)	0.25					0.5					1.0					2.5				
Outlet Temperature, °C	59 ± 1					59 ± 1					59 ± 1					59 ± 1				
Power Ratio, kW/kg	1.3					1.3					1.3					1.3				
	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)
	25	65	50	90		25	65	50	90		25	65	50	90		25	65	50	90	
1	45.0	172.0	11.4	58.1	0.84	40.5	166	9.8	47.1	0.70	48.1	159.4	11.5	46.9	0.92	28.3	101.2	13.9	51.3	0.74
2	41.0	158.1	12.1	54.5	0.82	46.6	175	12.1	56.1	0.75	37.4	134.1	13.2	49.7	0.99	29.8	103.7	13.9	51.0	0.79
3	55.2	194.8	8.7	35.1	0.92	53.1	172	8.0	30.8	0.68	29.4	93.6	10.3	29.2	0.90	34.7	107.5	10.3	33.8	0.75
4	39.0	141.7	9.3	29.9	0.81	36.9	129	9.1	40.0	0.60	31.1	99.9	10.6	32.7	0.80	23.8	77.9	13.2	14.5	0.66
5	58.7	249.2	7.5	29.2	1.18	57.7	195	8.8	40.0	0.83	46.6	183.4	8.8	37.8	1.10	40.5	154.3	8.6	33.0	0.83
6	59.7	242.9	9.8	42.1	1.08	56.2	207	9.2	41.3	0.70	52.1	194.8	9.3	46.7	0.99	31.9	129.0	12.0	42.6	0.76
Average	49.8	193	9.8	41.5	0.94	48.5	174	9.5	42.6	0.71	40.8	144	10.3	40.5	0.95	31.5	112	12.0	42.7	0.76
Fatigue Loss (%)	9.2%					14.7%					5.2%					15.6%				

Table 31

Effect of Concentration of Blowing Agent on Properties of Polyimide Foams at an Outlet Temperature of 64 ± 1°C

Foam Number	184					183					182					185				
Blowing Agent (%)	0.25					0.5					1.0					2.5				
Outlet Temperature, °C	64 ± 1					64 ± 1					64 ± 1					64 ± 1				
Power Ratio, kW/kg	1.3					1.3					1.3					1.3				
	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)
	25	65	50	90		25	65	50	90		25	65	50	90		25	65	50	90	
1	47.1	184.7	16.0	54.8	1.03	48.6	184.7	11.8	38.6	1.03	39.5	151.8	14.0	53.3	0.94	31.4	105	15.1	61.2	0.79
2	42.5	164.4	16.6	54.1	0.95	37.2	149.3	13.9	46.3	0.95	31.4	121.4	11.9	53.0	0.81	30.9	118.9	15.2	55.8	0.77
3	64.8	216.3	11.9	31.5	1.16	54.6	187.2	9.2	24.3	1.07	44.0	150.5	10.6	31.0	0.89	28.8	89.8	11.3	40.5	0.69
4	43.5	153.5	10.7	30.7	1.00	46.0	163.2	10.5	33.3	0.93	32.4	112.6	13.6	38.0	0.75	26.3	82.0	9.4	33.1	0.62
5	58.2	221.4	10.7	29.7	1.33	58.2	222.6	9.0	33.0	1.29	43.5	160.7	12.7	42.5	0.98	35.2	111.3	12.1	38.6	0.91
6	65.8	260.6	13.4	38.9	1.23	59.7	220.1	10.8	42.3	1.19	47.6	191.0	12.3	41.4	1.01	33.1	108.8	10.9	33.6	0.82
Average	53.6	200	13.2	39.9	1.12	50.7	188	10.9	36.3	1.08	39.7	148	12.5	43.2	0.90	30.95	102	12.3	43.8	0.77
Fatigue Loss (%)	1.6%					4.3%					3.1%					8.2%				

Table 32

Effect of Concentration of Blowing Agent on Properties of Polyimide Foams at an Outlet Temperature of 69 ± 1°C

Foam Number	219					220					221					222				
Blowing Agent (%)	0.25					0.5					1.0					2.5				
Outlet Temperature, °C	69 ± 1					69 ± 1					69 ± 1					69 ± 1				
Power Ratio, kW/kg	1.3					1.3					1.3					1.3				
	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)
	25	65	50	90		25	65	50	90		25	65	50	90		25	65	50	90	
1	66.3	263	12.0	54.5	1.22	49.3	192	13.3	61.8	1.06	42.0	161	16.7	62.2	0.96	38.0	134	12.4	46.5	0.89
2	51.6	204	12.8	51.7	1.13	46.1	172	15.1	58.4	1.09	41.2	157	13.0	66.3	0.98	34.2	121	13.7	53.8	0.88
3	86.0	352	11.9	37.2	1.56	66.3	233	9.4	46.6	1.35	49.3	176	10.9	43.1	1.01	52.4	164	9.7	30.2	1.07
4	65.8	258	9.4	25.7	1.16	68.3	233	8.5	26.1	1.18	33.6	121	11.9	47.6	0.88	25.3	94.9	11.2	33.1	0.99
5	76.9	330	10.2	45.6	1.36	66.0	260	9.3	43.3	1.33	51.1	216	11.1	52.2	1.00	54.6	207	14.0	50.3	1.29
6	76.9	334	12.1	37.0	1.32	89.1	347	10.0	37.0	1.40	51.1	201	10.3	55.2	1.02	52.1	221	10.0	43.0	1.17
Average	70.6	290	11.4	42.0	1.20	64.2	240	10.9	45.5	1.24	44.7	172	12.3	54.5	0.99	42.8	157	11.8	42.8	1.05
Fatique Loss (%)	0%					2.9%					1.6%					2.2%				

Table 33

Effect of Concentration of Blowing Agent on Properties of Polyimide Foams at an Outlet Temperature of 74 ± 1°C

Foam Number	286					291					290					287				
Blowing Agent, (%)	0.25					0.5					1.0					2.5				
Outlet Temperature, °C	74 ± 1					74 ± 1					74 ± 1					74 ± 1				
Power Ratio, kW/kg	1.3					1.3					1.3					1.3				
	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)	ILD (lbf)		CS (%)		D (lbs/ft^3)
	25	65	50	90		25	65	50	90		25	65	50	90		25	65	50	90	
1	79.4	339.0	18.5	64.7	1.38	71.4	355	12.9	41.7	1.79	80.0	327	12.3	50.0	1.28	57.7	245.4	14.5	57.0	1.36
2	68.8	316.3	18.5	63.3	1.26	60.4	369	12.1	39.6	1.56	55.2	223	18.5	63.2	1.22	60.7	240.4	15.0	45.0	1.27
3	90.1	339.0	13.3	57.4	1.80	105	516	12.0	40.9	2.08	82.5	367	13.2	45.8	1.60	60.7	232.8	14.9	46.9	1.47
4	87.0	344.1	15.7	48.3	1.56	91.1	362	13.6	49.2	1.70	68.8	321	16.2	39.7	1.33	50.6	179.6	17.8	61.7	1.06
Average	81.3	335	16.5	58.4	1.50	87.0	400	12.6	42.8	1.78	71.6	310	13.0	49.7	1.36	57.4	225	15.6	52.6	1.29
Fatigue Loss (%)	1.0%					1.3%					1.3%					1.4%				

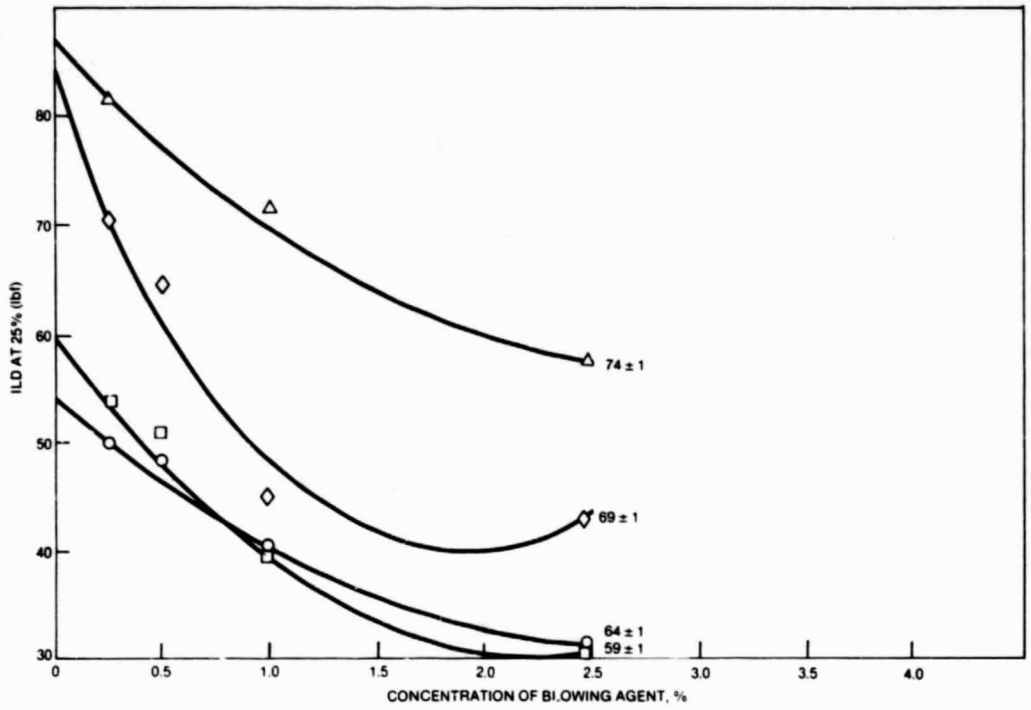


Figure 62. Effect of Concentration of Blowing Agent on the ILD Values of Polyimide Foams Produced From Precursors Dried at Various Outlet Temperatures

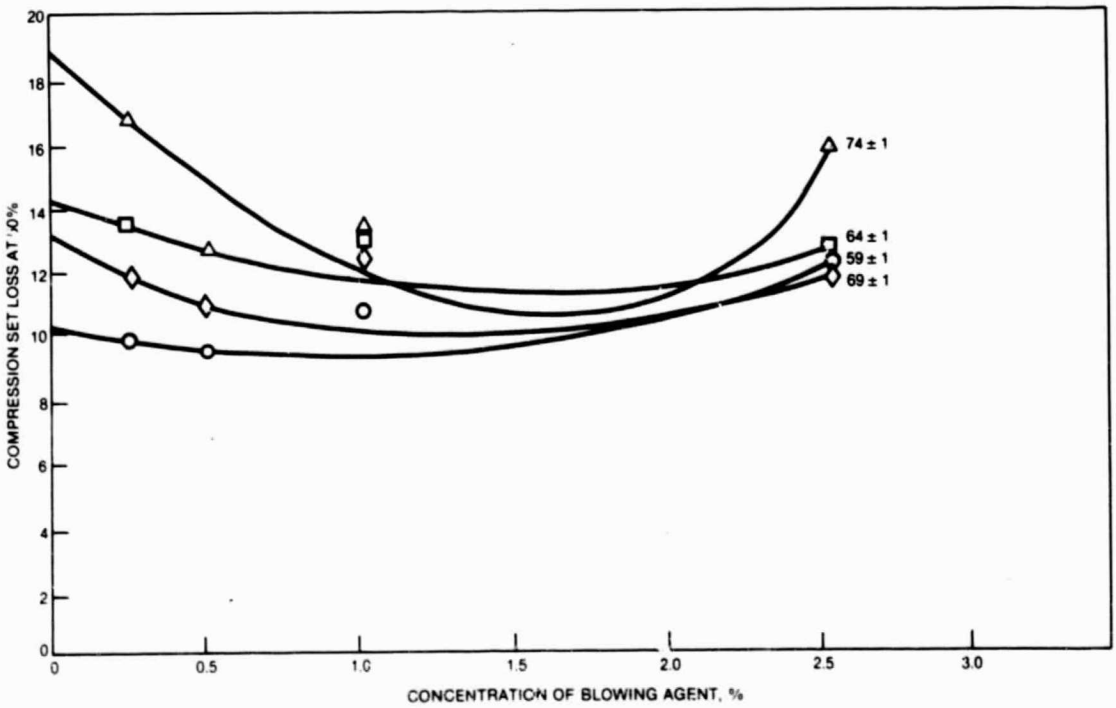


Figure 63. Effect of Concentration of Blowing Agent on the Compression Set Loss of Polyimide Foams Produced From Precursors Dried at Various Outlet Temperatures

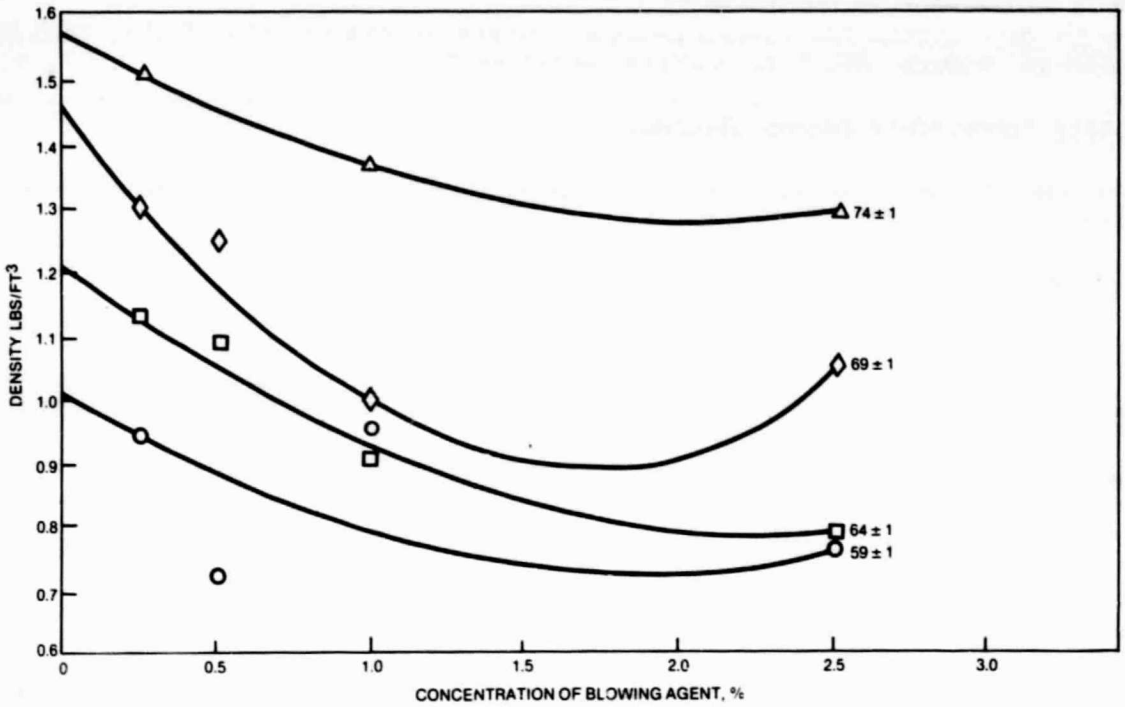


Figure 64. Effect of Concentration of Blowing Agent on the Density of Polyimide Foams Produced From Precursors Dried at Various Outlet Temperatures

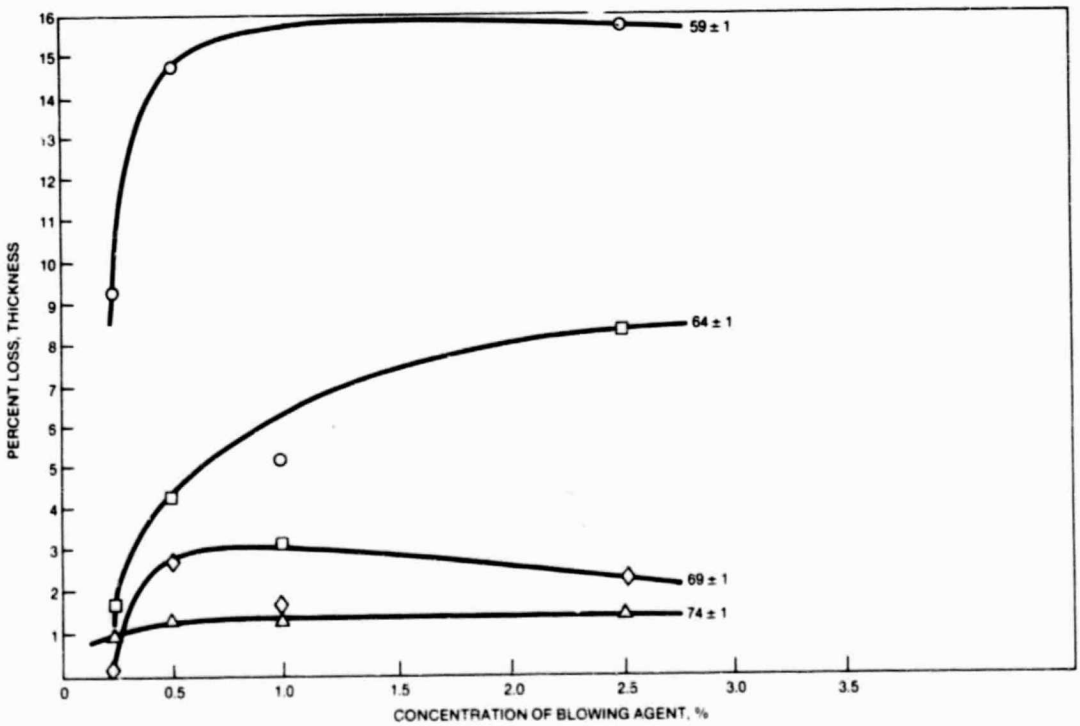


Figure 65. Effect of Concentration of Blowing Agent on the Fatigue Resistance of Polyimide Foams Produced From Precursors Dried at Various Outlet Temperatures

Foams produced with the advanced and optimized process at the four temperature ranges were tested for cyclic fatigue resistance and results of this test are shown in Figure 66. To better understand the properties of polyimide foams, Comfort Index and percent open cell were also measured for each of the outlet temperature ranges studied.

The comfort index or sag factor is defined as the ratio of the ILD at 65 percent and the ILD at 25 percent.

$$\text{Comfort Index (CI)} = \frac{65\% \text{ ILD}}{25\% \text{ ILD}}$$

A low CI value indicates that the foam will bottom out resulting in inferior performance. A high CI value indicates a very stiff foam which would be uncomfortable. For the best seating comfort, the CI values should be in the range of 2.0 to 6.0. Table 34 lists the CI values for a series of foams produced from powder resin spray dried at the four temperature ranges and foamed with varying amounts of blowing agent.

The data show that the comfort index is slightly affected by the spray dryer outlet temperature, the higher the temperature the higher the comfort index with very little affect shown by the concentration of blowing agent. It can also be concluded that the comfort index of the polyimide foams varies within a narrow range of values with critical changes of process parameters.

Figure 66. Effect of Outlet Temperature on Fatigue Resistance of Polyimide Foams From Top to Bottom (74 ±1, 69 ±1, 64 ±1 and 59 ±1°C)

Table 34

Comfort Index of Polyimide Foams

Spray Dryer Temperature (°C)	Concentration of Blowing Agent (%)				Average of All Blowing Agent Concentrations
	0.25	0.50	1.0	2.5	
59 ± 1	3.8	3.6	3.6	3.5	3.6
64 ± 1	3.8	3.8	3.8	3.5	3.7
69 ± 1	4.1	3.8	4.0	3.7	3.9
74 ± 1	4.4	4.3	4.2	3.9	4.2

The open cell content of a foam was measured initially to determine the effectiveness of various techniques used to obtain low ILD at 25 percent deflection. Table 35 lists the open cell content of the foams discussed in this section which were produced at various concentrations of blowing agents from powders spray dried at the four outlet temperatures. These data show that the concentration of blowing agent has no clear effect on the open cell content. The outlet temperature, however has a significant effect on the percent open cell content. This is due to the lower volatile content of the powder resin which the blowing agent is not able to replace. With this study the evaluation of the open cell content by Air Pycnometer readings was discontinued, but this property will continue to be measured as a monitor for process controls.

Table 35

Percent Open Cell of Polyimide Foams

Outlet Temperature (°C)	Concentration of Blowing Agent (%)			
	0.25	0.50	1.0	2.5
59 ± 1	98.0	97.7	97.9	97.7
64 ± 1	96.[illegible]	97.3	97.6	97.0
69 ± 1	96.6	97.5	98.3	97.9
74 ± 1	93.3	95.3	96.4	95.6

Task III - Optimization of Foaming Parameters - Summary

1. A polypropylene square open mold configuration with bottom grid, corner vents, polyimide insulation, and perforated top has been selected as the standard tool for all foaming operations.

2. Efforts of this task have resulted in the selection of the following optimized foaming parameters:

Powder Loading	=	8.235 kg (18 lbs)
Power Ratio (foaming)	=	1.3 kW/kg
Curing Power	=	14 kW
Microwave Curing Time	=	42.0 minutes
Pulsing Cycle	=	20/20

3. Crushing technique was selected to obtain lower ILD values and improve flexibility of the foams.

4. Efforts of this task have resulted in identification of processing and compositional parameters which regulate the ILD values of the foams and provide methods to achieve a classification into specific products. These parameters are:

   - Outlet temperature
   - Concentration of blowing agent
   - Crushing technique

5. Properties of polyimide foam products have been defined at these processing and compositional parameters to help the classification of foams according to established ILD values.

4.4 TASK IV - POLYIMIDE FOAMS EVALUATION AND CLASSIFICATION

The major objective of this task is to determine relationships between the most critical properties of the foams and processing parameters and compositions. The relationships are then employed to classify the foams into products in accordance with the program goal.

This section is divided into three parts to improve clarity. A discussion of the data generated is presented in the following sequence.

1. Identification of Classes
2. Stress-Strain Relationships/Comfort Index
3. Properties Evaluation

4.4.1 Task IV - Identification of Classes

This task is divided into three sections for clarity. These sections are:

i. Identification of achievable class ranges

ii. Identification of foams consistent with class ranges

iii. Identification of process parameters and compositions which yield foams consistent with class ranges

Identification of Achievable Class Ranges

In Task II the dependence of foam properties as a function of the spray drier outlet temperature and blowing agent concentration was discussed. These data are graphically presented in Figure 67 where the average and scatter of ILD values at 25 percent deflection are represented by circles and vertical bars respectively. As shown in this figure, the ILD values at 25 percent deflection are directly proportional to the outlet temperature and inversely proportional to the concentration of blowing agent.

Superimposition of the ILD requirements of the five classes upon Figure 67 is shown in Figure 68. This figure compares the wide variability of the ILD properties of the polyimide foams with the narrow requirements set forth in the program proposal.

At the conclusion of this effort the following achievable ILD ranges at 25 percent deflection were established for each of the five classes. These ranges are illustrated in Figure 69.

	ILD at 25% Deflection	
Class	Established	Goal
I	15-25	18
II	25-40	24
III	40-50	44
IV	50-60	50-55
V	70-80	70-80

An examination of Figure 69 indicates that powder precursors spray dried at 59 $\pm$ 1°C and 74 $\pm$ 1°C (138.2°F and 165.2°F) produce foams falling within two classes, while powder precursors spray dried at 64 $\pm$ 1°C and 69 $\pm$ 1°C (147.2°F and 156.2°F) yield foams falling within three or more classes. Figure 69 also shows that Class II foams possessing an ILD value in the range of 25-40 can be obtained through variation of compositions and/or processing parameters, but Class I foams possessing an ILD in the range of 15-25 are not easily achievable through the same process or compositional changes.

This deficiency has been resolved as discussed in the following subsection.

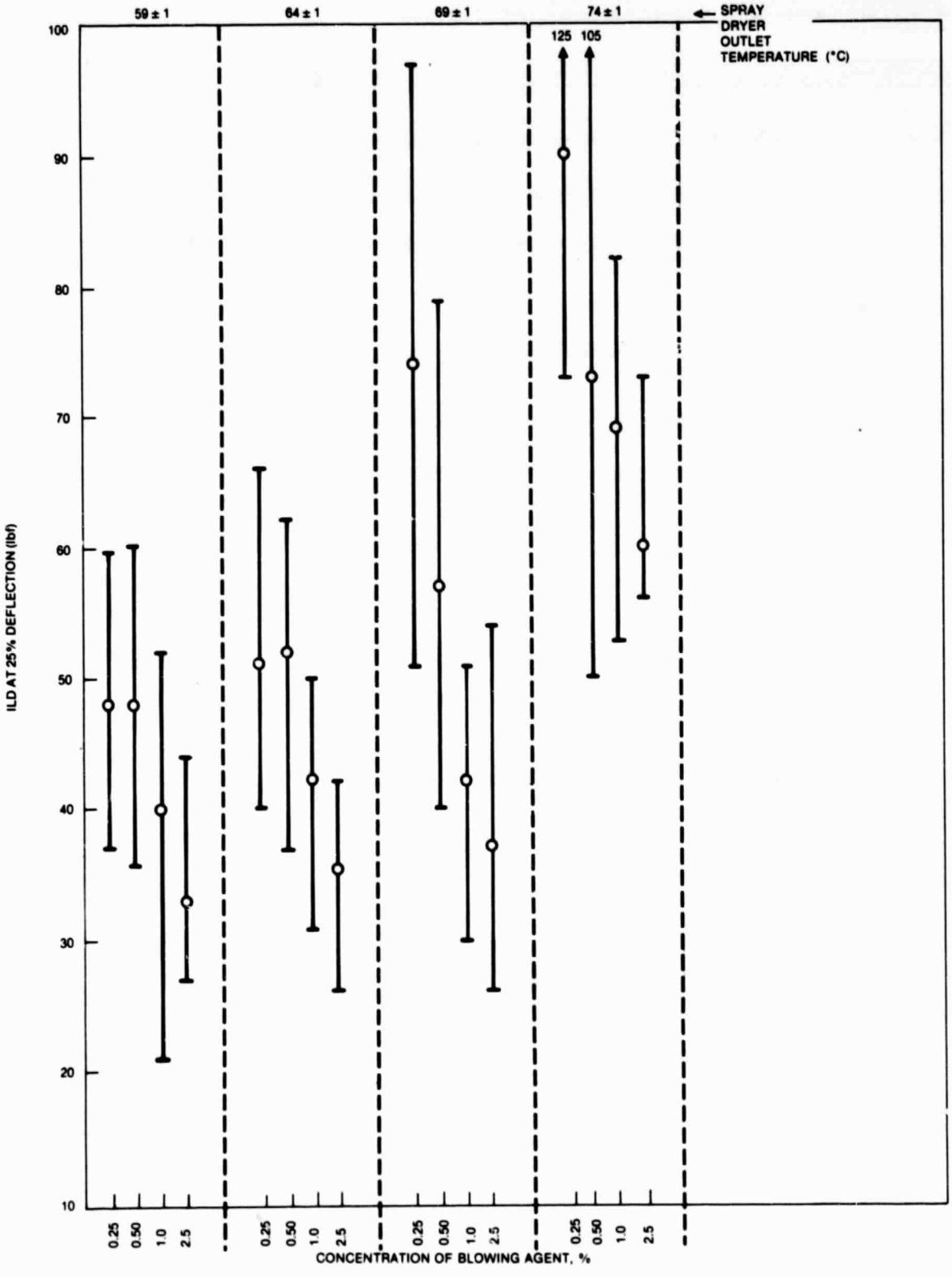


Figure 67. Classification of Foams Based on ILD at 25% Deflection

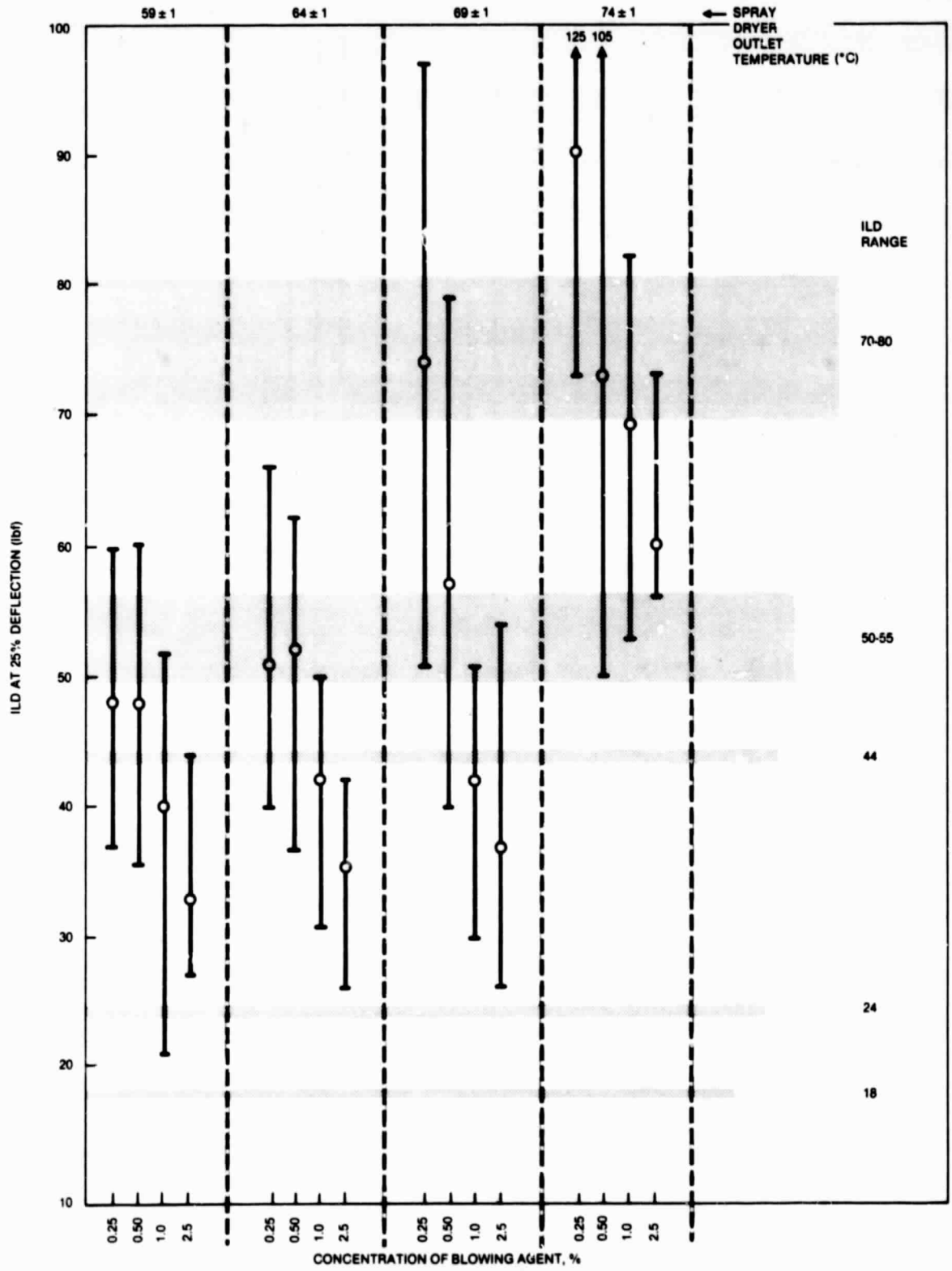


Figure 68. Classification of Foams Based on ILD at 25% Deflection

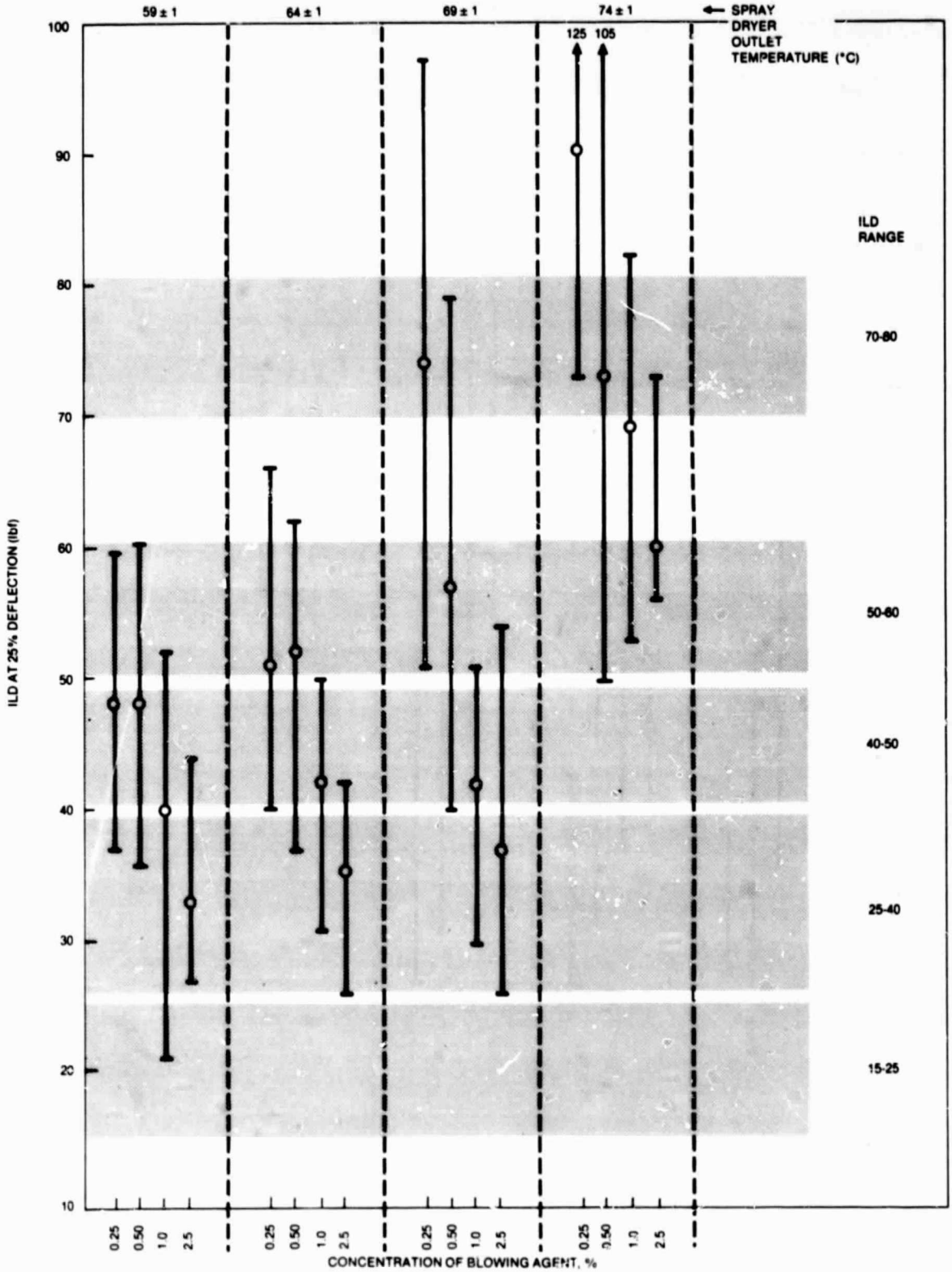


Figure 69. Classification of Foams Based on ILD at 25% Deflection

Identification of Foams Consistent With Class Ranges

As discussed in the preceding sections, it was not possible to achieve five classes of polyimide foams through a single process variable, specifically the spray drying temperature. The two most promising temperatures were 64 ± 1 and 69 ± 1°C (147.2°F and 156.2°F) which yielded three and four classes of foams respectively. To produce Class I and Class II foams another process modification was introduced. This process involved crushing the foams after the final thermal cure as discussed in Task III. This process lowers the ILD values of the foams to values meeting the requirements of Class I and II. The results of this study are shown in Figure 70 which is obtained by superimposing the data on Figure 69. The foams used for the crushing study were produced from powder precursors made at an outlet temperature of 69 ± 1°C (156.2°F) using a blowing agent concentration of 2.5 percent. This concentration was selected because it consistently produced foams with lowest ILD values at 25 percent deflection. As reported previously, this temperature generated more classes of foams than any other spray drying temperature studied. The data presented in Figure 70 is summarized in Table 36 where the conditions to achieve each class are clearly identified.

Identification of Process Parameters and Compositions Which Yield Foams Consistent With Class Ranges

A summary of all the spray drying temperatures studied and their effcts on powder precursors and foam properties is shown in Table 37. The data show that a temperature of 69 ± 1°C (156.2°F) yields powder precursors which produce foams possessing good fatigue properties, homogeneity within and between buns, and moderate compression set loss.

Examination of Table 36 and Figure 70 clearly illustrates that a spray drying temperature of 69 ± 1°C (156.2°F) yields all five classes of polyimide foams according to ILD values at 25 percent deflection by combinations of blowing agent concentration and crushing technique.

From the review of all the data previously presented, 69 ± 1°C (156.2°F) was selected as the optimum outlet temperature condition for the production of polyimide foams meeting the ILD requirements of all five classes in accordance with the program goal.

The final processing parameters and compositions for each of the five classes selected in this task are reported in Table 38.

4.4.2 Compressive Stress-Strain Relationships/Comfort Index

The objective of this subtask was to measure and evaluate the effect of processing parameters on compressive stress-strain relationship. This study was expected to result in a clearer understanding of the physical properties of polyimide foams leading to appropriate specifications. Investigation of

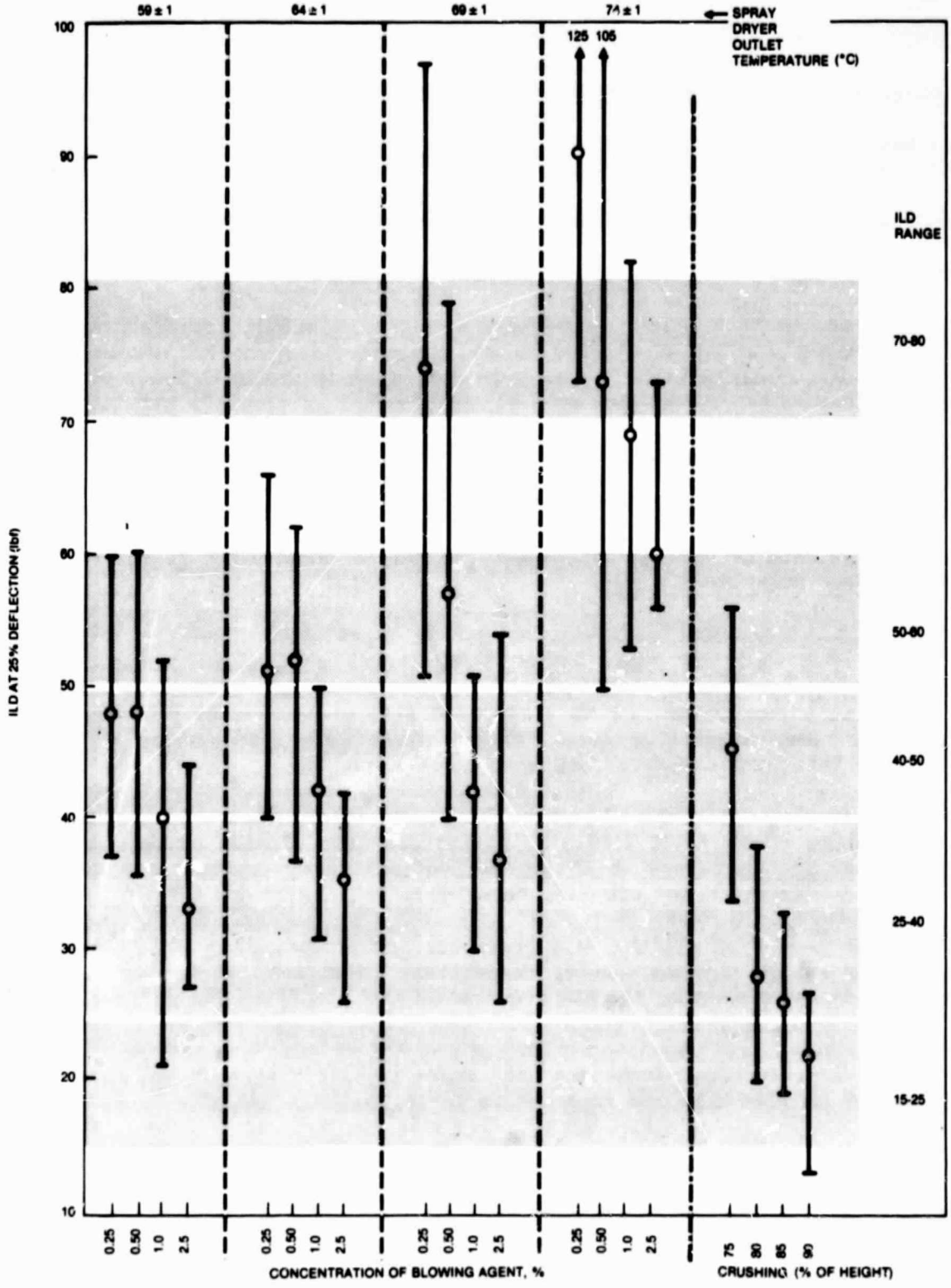


Figure 70. Classification of Foams Based on ILD at 25% Deflection

Table 36

Summary of Process Parameters Studied to Obtain Various Classes

Class	I	II	III	IV	V
ILD Range (lbf)	15 - 25	25 - 40	40 - 50	50 - 60	70 - 80
Process Parameters		59 ± 1 1.0% BL* 2.5% BL 64 ± 1 1.0% BL 2.5% BL	59 ± 1 0.25% BL 0.50% BL 64 ± 1 0.25% BL 0.50% BL		
	69 ± 1 2.5% BL 90% crush	69 ± 1 2.5% BL 80% crush	69 ± 1 1.0% BL	69 ± 1 0.5% BL 74 ± 1 2.5% BL	69 ± 1 0.25% BL 74 ± 1 0.25% BL 0.50% BL 1.0% BL
*BL = Blowing Agent					

these relationships were undertaken in two complimentary studies through measurements of indentation load deflection and compression set loss values.

The indentation load deflection (ILD) test is a measure of the force required to compress a foam sample to a designated deflection. In the present study the foam samples were compressed from 5 to 80 percent of the original height by the method described in ASTM 3574-77, Test D. Data obtained in this test are tabulated in Table 39 for the effect of various outlet temperatures, concentrations of blowing agent and level of foam crushing.

The compression set test done in accordance with ASTM D 3574-77, Test D compresses foam samples to 90 and 50 percent of their initial height, maintaining them under compression for 22 hours. After 22 hours the load is removed and the samples are allowed to recover for 30 minutes, after which time the heights are remeasured and the amount of loss from the initial height is calculated. In this task, compressions of 90,80,70, 60, 50 and 30 percent were investigated. The foam samples were held under compression for 22 hours following which they were removed and remeasured at intervals of 30, 60, 90 minutes and 24 hours. A summary of this work is given in Table 40 which shows data for compression set losses at different compression levels and recovery periods for foams produced at various outlet temperatures and blowing agent concentrations. The data given in Table 39 are graphically presented in Figures 71, 72, 73 and 75 and the data given in Table 40 graphically presented in Figure 76.

Table 37

Properties of Foams Produced at Various Spray Dryer Outlet Temperatures

Spray Dryer Temperature (°C)	Fatigue Loss (%)	Relative Yield	Benefits	Problems
59 ± 1	4.1 - 15.6	High	High production rate Good C.S. Soft foam Low dust (heavy powder) Low C.I.	Poor fatigue Poor homogeneity Two classes at most
64 ± 1	1.6 - 8.2	Very good	Good - high production rate Fair C.S. Soft Foam Moderate-low dust	Two classes at most Fair homogeneity Fair - poor fatigue
69 ± 1	0 - 4.5	Good	Moderate C.S. Good fatigue Three to four classes Moderate low ILD Improved homogeneity	Fair - poor production Dusty Slightly higher C.S.
74 ± 1	0.5 - 1.0	Poor	Excellent fatigue	Lowest production Very dusty Collapses during curing Worst C.S. High C.I. Only one class Poor homogeneity

Figures 71 and 72 illustrate the ILD values of foams produced using various combinations of these parameters. At ILD deflection levels less than 50 percent the curves representing foams made at different blowing agent concentrations are better differentiated than the curves representing foams made from powder precursors spray dried at various outlet temperatures. As a result the definition of the foam classes is better achieved through variation of blowing agent concentrations.

The effects of crushing on the ILD values are shown in Figure 73. A foam with a low ILD value would be expected to maintain this low property throughout the entire strain range, however, polyimide foams which have been crushed do not exhibit this property, but tend to have higher stress at deflection levels greater than 50 percent.

As shown in Figures 71, 72 and 73, polyimide foams are characterized by very rapid increases in stress when the strain exceeds 50 percent. This is in direct contrast to conventional polyurethane foams which do not exhibit the same type of increase until a deflection value higher than 65 percent is reached. This different behavior is shown in Figure 74. This difference in properties is also reflected by the polyimide and polyurethane foams seating properties. Polyurethane foams will commonly compress to 80 to 90 percent of their initial height under the generally accepted weight of 200 pounds,

Table 38

Selection of Process Parameters and Compositions
for Various Classes

Class	I	II	III	IV	V
Synthesis					
Resin	1720-1	1720-1	1720-1	1720-1	1720-1
Reaction Temperature (°C)	60-65	60-65	60-65	60-65	60-65
Surfactant Concentration (%)	0.75	0.75	0.75	0.75	0.75
Spray Drying					
Inlet Temperature (°C)	100	100	100	100	100
Outlet Temperature (°C)	69 ± 1	69 ± 1	69 ± 1	69 ± 1	69 ± 1
Dilution Ratio, phr	30	30	30	30	30
Microwave Foaming					
Blowing Agent (%)	2.5	2.5	1.0	0.5	0.25
Powder Load (kg)	8.235	8.235	8.235	8.235	8.235
Foaming Power (kW)	10.7	10.7	10.7	10.7	10.7
Foaming Power Ratio (kW/kg)	1.3	1.3	1.3	1.3	1.3
Microwave Pulsing	20/20	20/20	20/20	20/20	20/20
Foaming Time (min.)	23	23	23	23	23
Curing Power (kW)	14	14	14	14	14
Curing Time (mins.)	40	40	40	40	40.5
Thermal Curing					
Curing Temperature (°C)	177-246	177-246	177-246	177-246	177-246
(°F)	350-475	350-475	350-475	350-475	350-475
Curing Time (mins.)	80	80	85	90	90
Crushing (%)	95	85	75	75	75

whereas polyimide foams will only compress to 70 percent of their initial height, under the same weight, as shown in Figure 75.

As shown by the data points, polyimide foams exhibit a very soft feel upon initial contact with the stress increasing progressively as the strain increases. In contrast, polyurethanes are initially quite firm maintaining a near flat response to increasing strain up to 65 percent deflection. This behavior is reflected by the comfort index factor of both types of foams. The comfort index, as discussed in Task III, is defined by the ratio between the ILD values at 25 and 65 percent deflection and indicates the relative comfort of seating foams. Table 41 summarizes the comfort index value of foams fitting the five classes selected. Polyimide foams meet the currently acceptable industrial criteria of 2 to 6 for comfort index values although Class I and II foams exhibit values in the high range of the scale.

Table 39

Indentation Load Deflection at Specified Deflections

Deflection Level (%)	Pound Force at Specified Deflections										
	5	10	20	25	30	40	50	60	65	70	80
Outlet Temperature (°C) (1.0% Blowing Agent)											
59 ± 1	12.1	23.5	37.2	44.0	50.6	65.3	85.0	116	142	180	364
64 ± 1	11.4	23.8	40.5	48.1	56.2	73.9	98.7	137	171	220	450
69 ± 1	11.6	25.3	44.0	52.6	61.7	82.0	110	156	196	261	597
74 ± 1	17.4	41.2	78.9	96.1	115	158	218	325	422	592	1418
Concentration of Blowing Agent, % [69 ± 1°C]											
0.25	12.6	38.7	85.0	108	129	176	238	354	458	627	1480
0.50	15.2	30.4	50.1	59.7	68.8	88.6	119	166	206	271	607
1.0	11.4	23.9	40.5	48.1	56.2	73.9	98.7	137	171	220	450
2.5	9.6	18.5	29.3	34.7	40.0	51.6	67.8	93.1	114	148	306
Crushing (2.5% Blowing Agent); [69 ± 1°C]											
80% for 10 times	6.3	11.6	21.8	26.1	30.9	46.6	64.8	105	137	202	536
90% for 16 times	4.6	8.9	17.2	21.0	25.3	35.4	49.6	74.9	98.7	139	387

Table 40

Percent Compression Set Loss at Specified Compressions

Recovery Time	30 min.	60 min.	90 min.	24 hrs	30 min.	60 min.	90 min.	24 hrs	30 min.	60 min.	90 min.	24 hrs	30 min.	60 min.	90 min.	24 hrs
% Compression	69 ± 1°C; 0.25% BL*				69 ± 1°C; 0.5% BL				69 ± 1°C; 1.0% BL				69 ± 1°C; 2.5% BL			
90	44.4	41.1	39.4	29.3	49.1	45.7	43.7	32.8	53.9	50.7	48.3	38.4	38.3	34.6	32.8	22.8
80	23.9	21.6	20.2	13.5	26.4	23.8	22.1	14.7	32.2	29.6	27.7	19.0	25.6	22.6	21.0	13.5
70	17.0	15.2	14.2	8.9	18.2	15.9	14.7	8.8	28.2	23.5	21.8	13.3	22.4	20.1	18.8	11.6
60	14.1	12.6	11.6	7.1	14.2	12.3	11.3	6.7	18.4	16.2	14.9	8.7	15.5	13.7	12.5	7.5
50	10.7	9.5	8.9	5.4	12.2	10.6	9.8	5.9	14.5	12.7	11.7	7.2	12.7	11.2	10.4	6.1
30	6.1	5.6	5.1	3.0	7.2	6.4	5.9	3.5	7.0	6.1	5.7	3.4	6.4	5.7	5.3	3.1
	59 ± 1°C; 1.0% BL				64 ± 1°C; 1.0% BL				69 ± 1°C; 1.0% BL				74 ± 1°C; 1.0% BL			
90	37.3	33.8	31.7	22.9	48.0	44.0	41.6	30.7	53.9	50.7	48.3	38.4	51.9	48.2	45.6	35.3
80	18.3	16.2	14.9	10.0	30.8	27.4	25.5	17.1	32.2	29.6	27.7	19.0	33.6	30.4	28.6	20.2
70	15.9	13.9	12.0	7.8	20.4	19.0	16.2	9.7	28.2	23.5	21.8	13.3	16.7	14.4	13.3	8.2
60	10.5	9.1	8.5	5.1	18.6	16.2	15.0	8.8	18.4	16.2	14.9	8.7	14.7	12.8	11.6	7.0
50	8.7	7.6	7.0	4.3	12.2	10.6	9.7	5.9	14.5	12.7	11.7	7.2	10.7	9.2	8.4	4.7
30	5.2	4.6	4.1	2.4	6.6	5.7	5.3	3.2	7.0	6.1	5.7	3.4	6.1	5.3	4.8	2.7

*BL = Blowing Agent

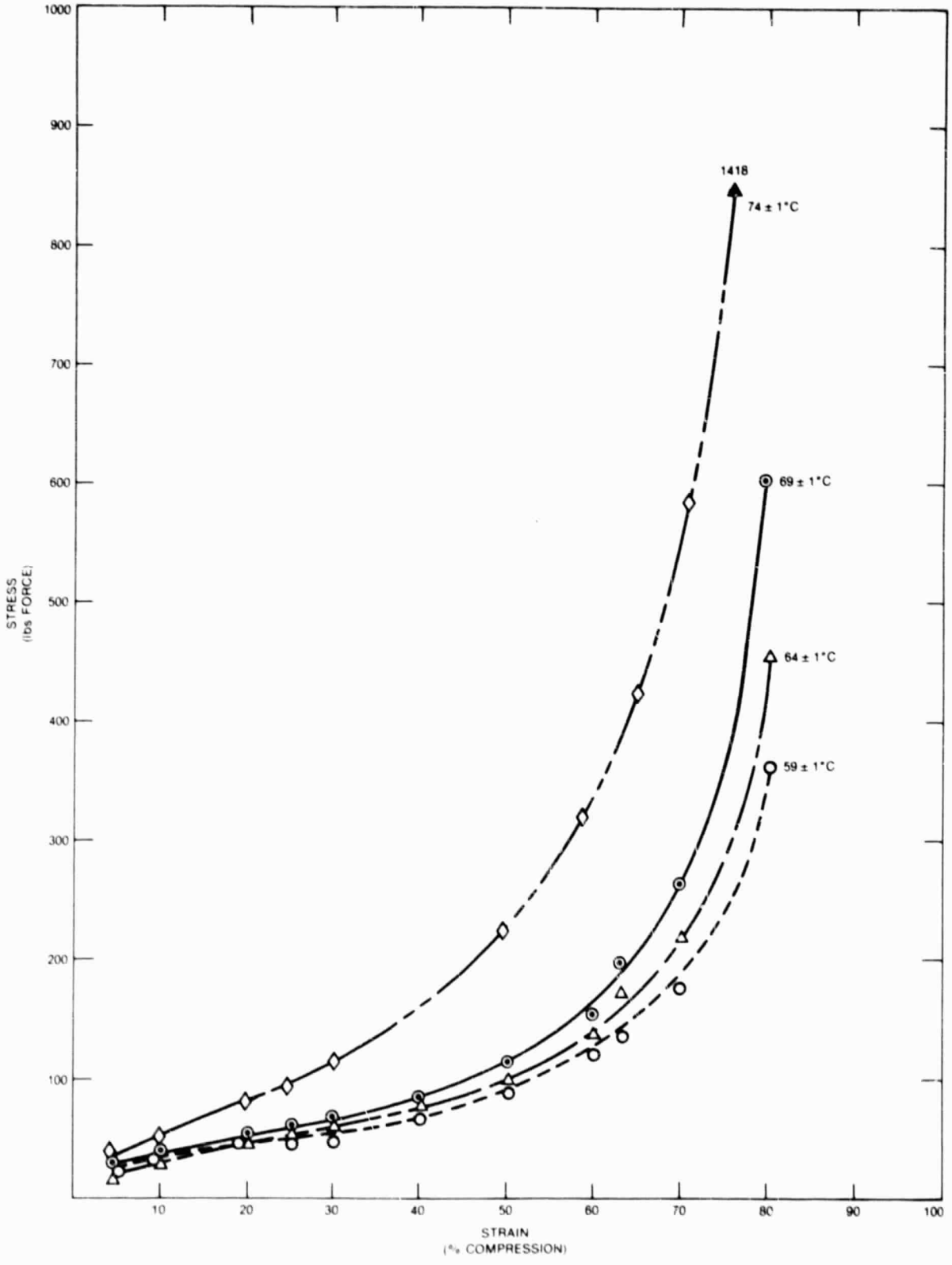


Figure 71. Compressive Stress-Strain Curves for Polyimide Foams Produced at Specified Spray Drier Outlet Temperatures

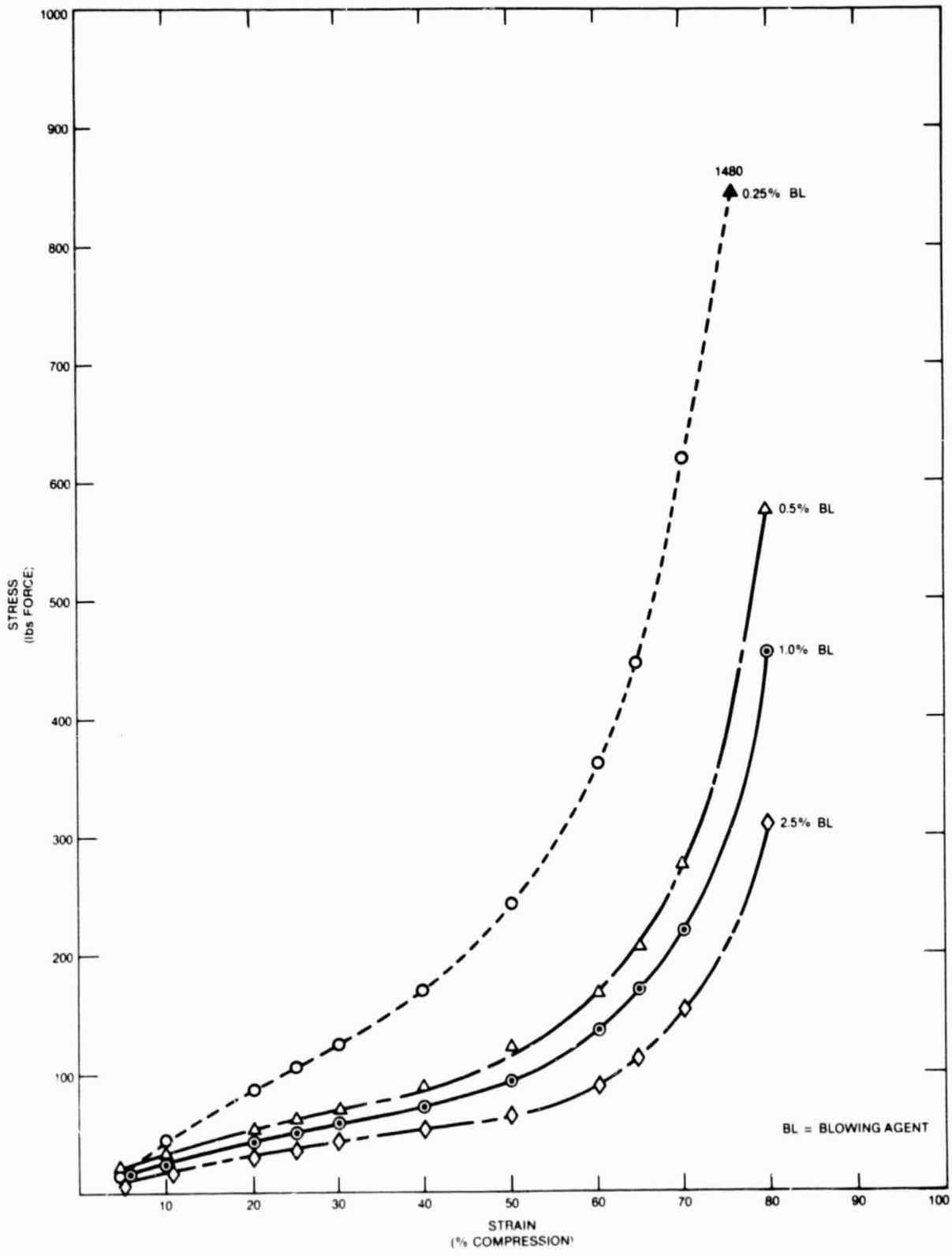


Figure 72. Compressive Stress-Strain Curves of Polyimide Foams Produced at Specified Concentrations of Blowing Agent

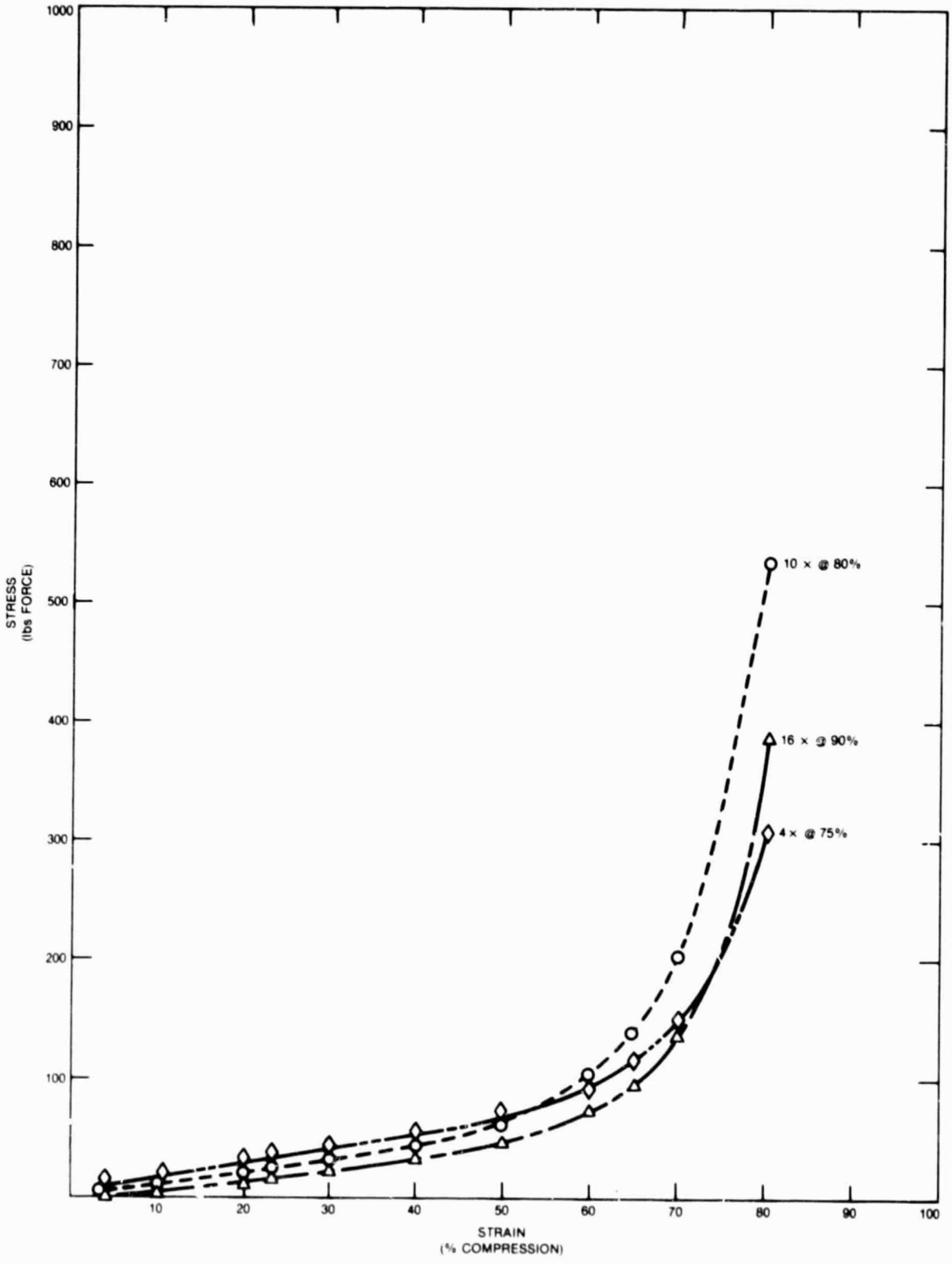


Figure 73. Compressive Stress-Strain Curves of Polyimide Foams After Crushing

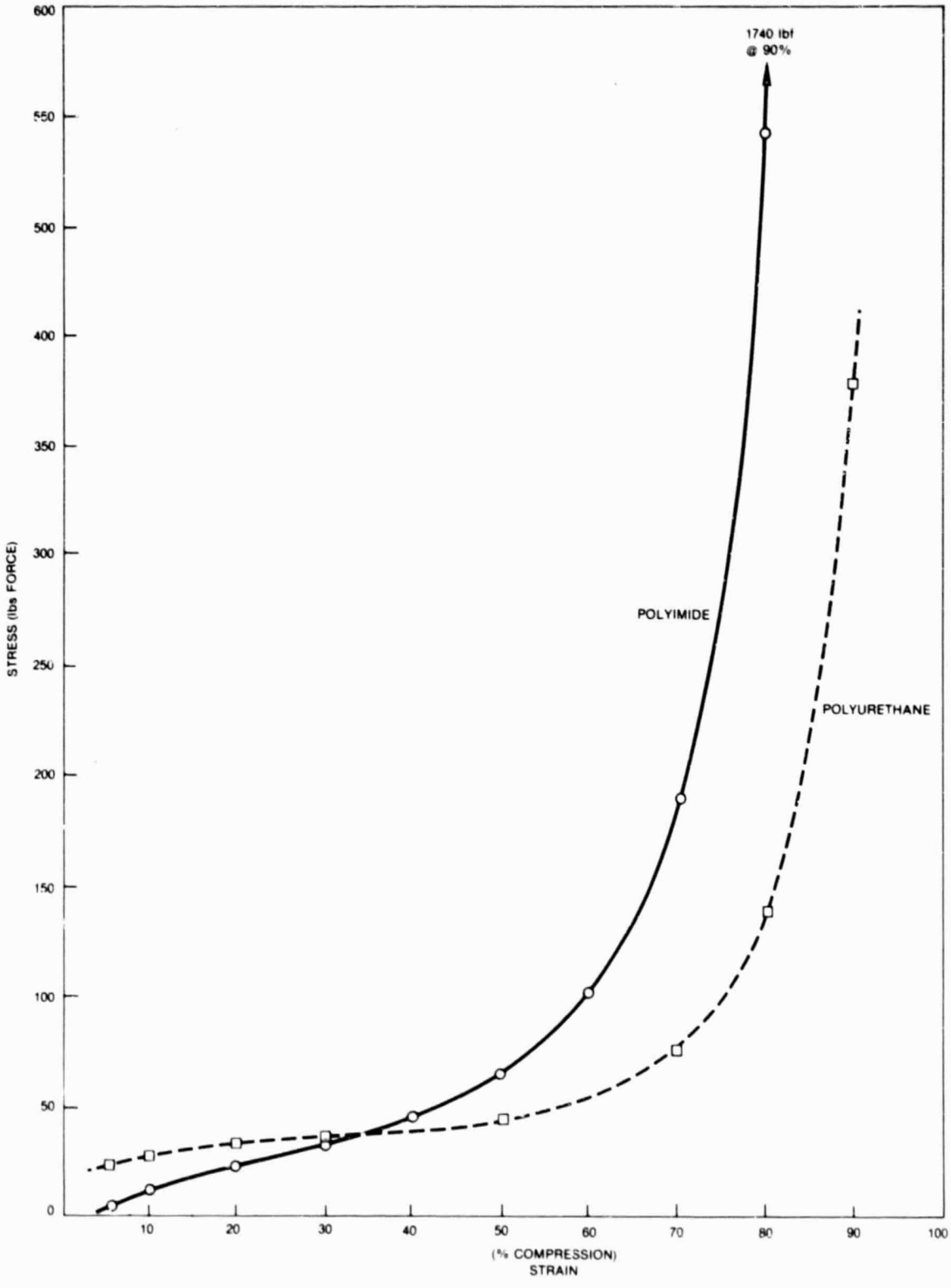


Figure 74. Comparison of Stress-Strain Curves of Polyurethane and Polyimide Foams, Class II

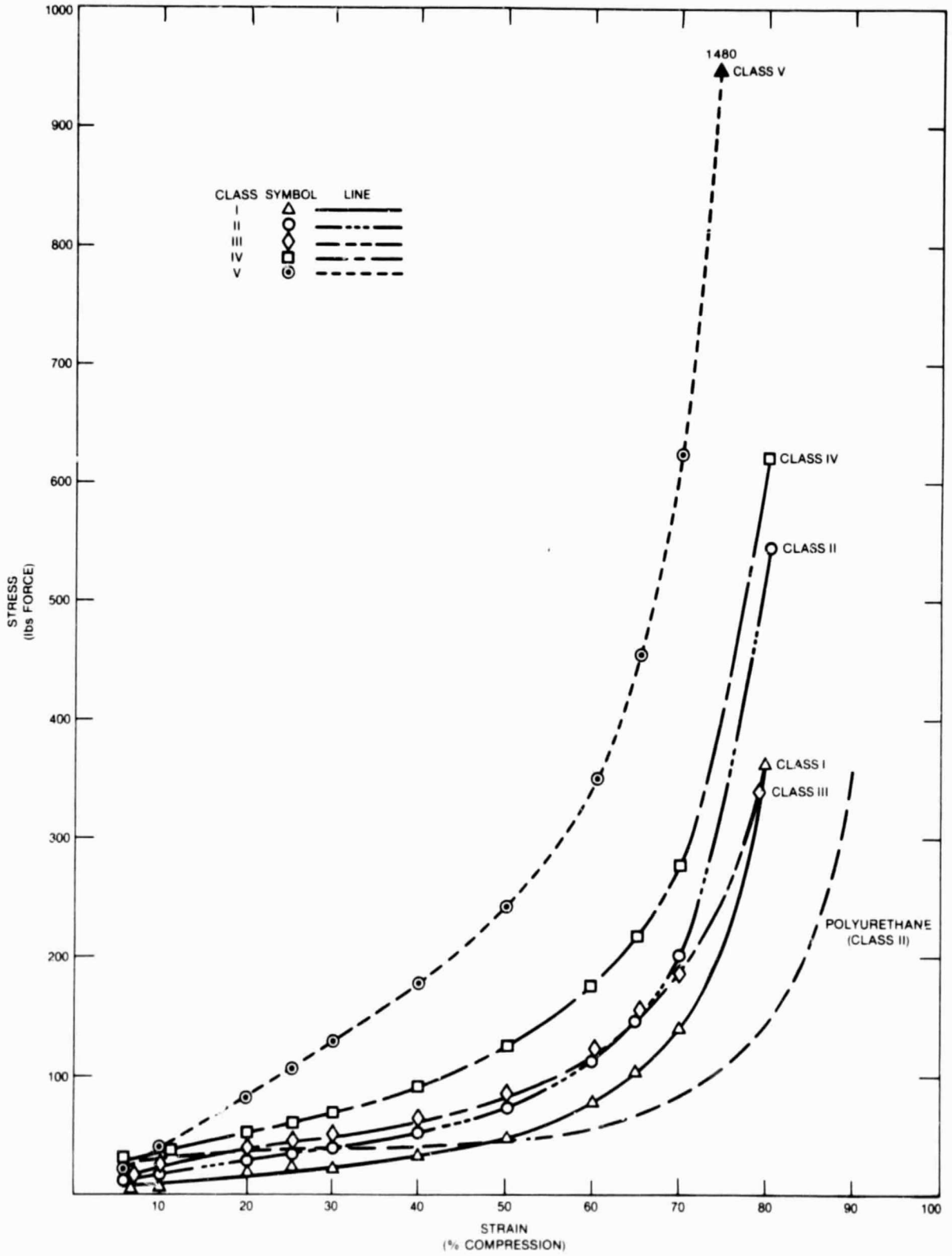


Figure 75. Comparison of Stress-Strain Curves of Class II Polyurethane and Class I. II, III, IV, and V Polyimide Foams

Table 41

Comfort Index of Polyimide Foams

ILD Class	ILD Class Range, lbf	Comfort Index
I	15-25	5.1
II	25-40	5.3
III	40-50	4.0
IV	50-60	3.8
V	70-80	4.1

The high comfort index value for polyimide foams, Classes I and II, is a result of the greater amount of "body" characteristics of polyimide foams which resist the "bottoming out" effect shown by polyurethane foams.

The molecular structure of polyimides is represented by a series of fused aromatic rings resembling the structure of a honeycomb. Conventional seating foams, have a linear long chain structure resembling coil springs. The honeycomb type structure is more resistant to deformation than the coil spring type structure, resulting in a greater degree of "body". This structure characteristic of polyimide foams is the major factor in its superior fire resistance properties. Another property affected by this honeycomb structure is compression set loss. As discussed in this section, this honeycomb structure resists deformation when a certain level of strain is reached. After this maximum strain level, the structure is broken or fractured resulting in slow compression set recovery. This effect is shown in Figure 76 where the values of compression set loss are shown at specified compression levels with individual lines plotted showing recovery after various lengths of time. The data points shown in Figure 76 indicate that polyimide foams possess the ability to recovery after release of stress over a long period of time, the rate of recovery being considerable for the first 30 minutes with additional recovery continuing through 60 minutes. After 60 minutes the rate of recovery is slow, continuing for at least 24 hours. In contrast conventional polyurethane foams recover quickly due to the elastic behavior of their coil spring type molecular structure which is also responsible for the high flammability. This is shown in Figure 77 where the compression set loss values for polyimide and polyurethane foams after 60 minutes recovery are shown.

The compression set losses for the various foam classes after 60 minutes recovery are shown in Figure 78. In summary, the compression set properties of conventional polyurethane foams are superior to those of polyimide foams. Conventional polyurethane foams are thermoplastic material which possess high elastic properties enabling them to recover from a compressed

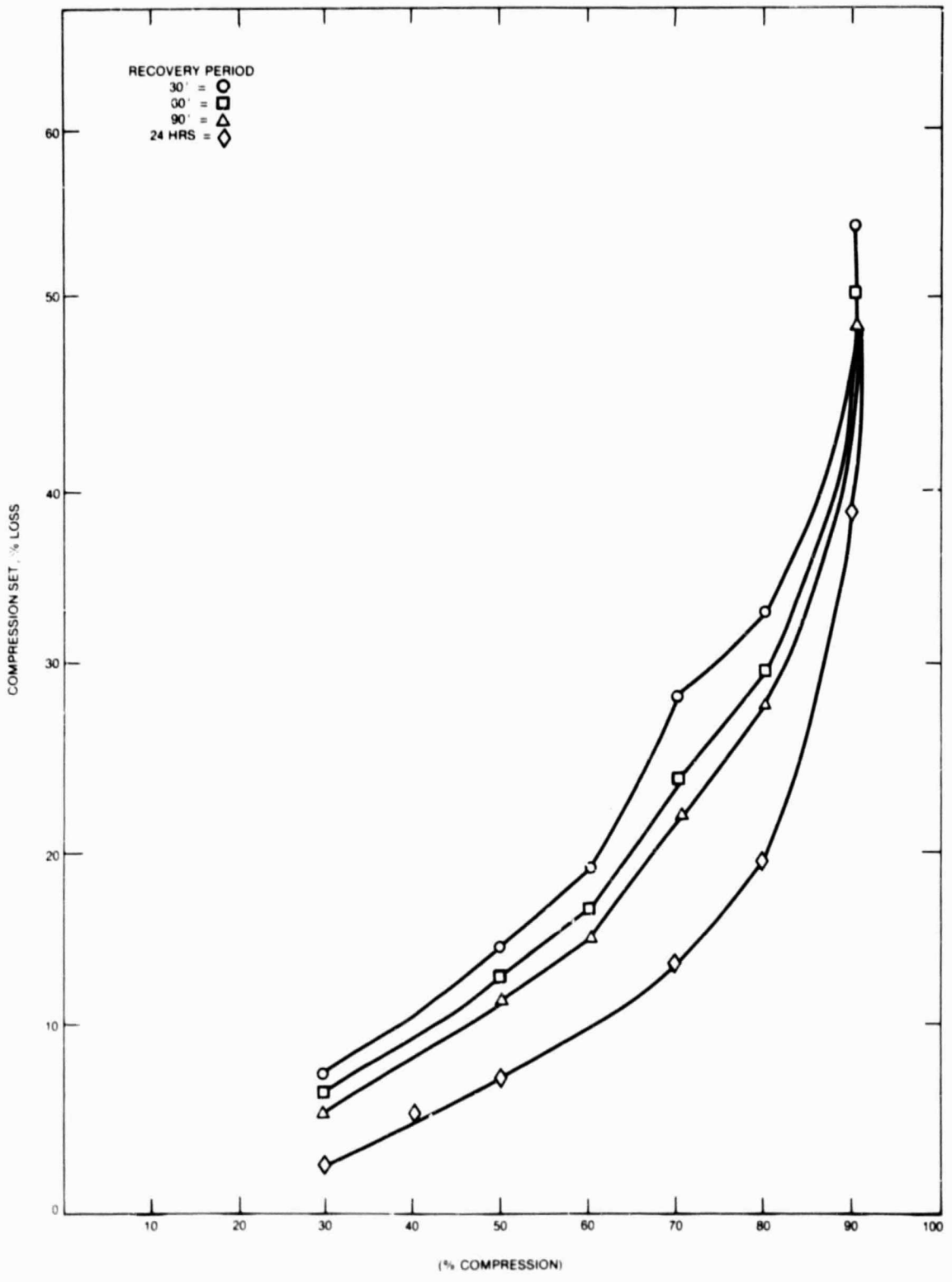


Figure 76. Compression Set Recovery Rate of Foams at Specified Compressions

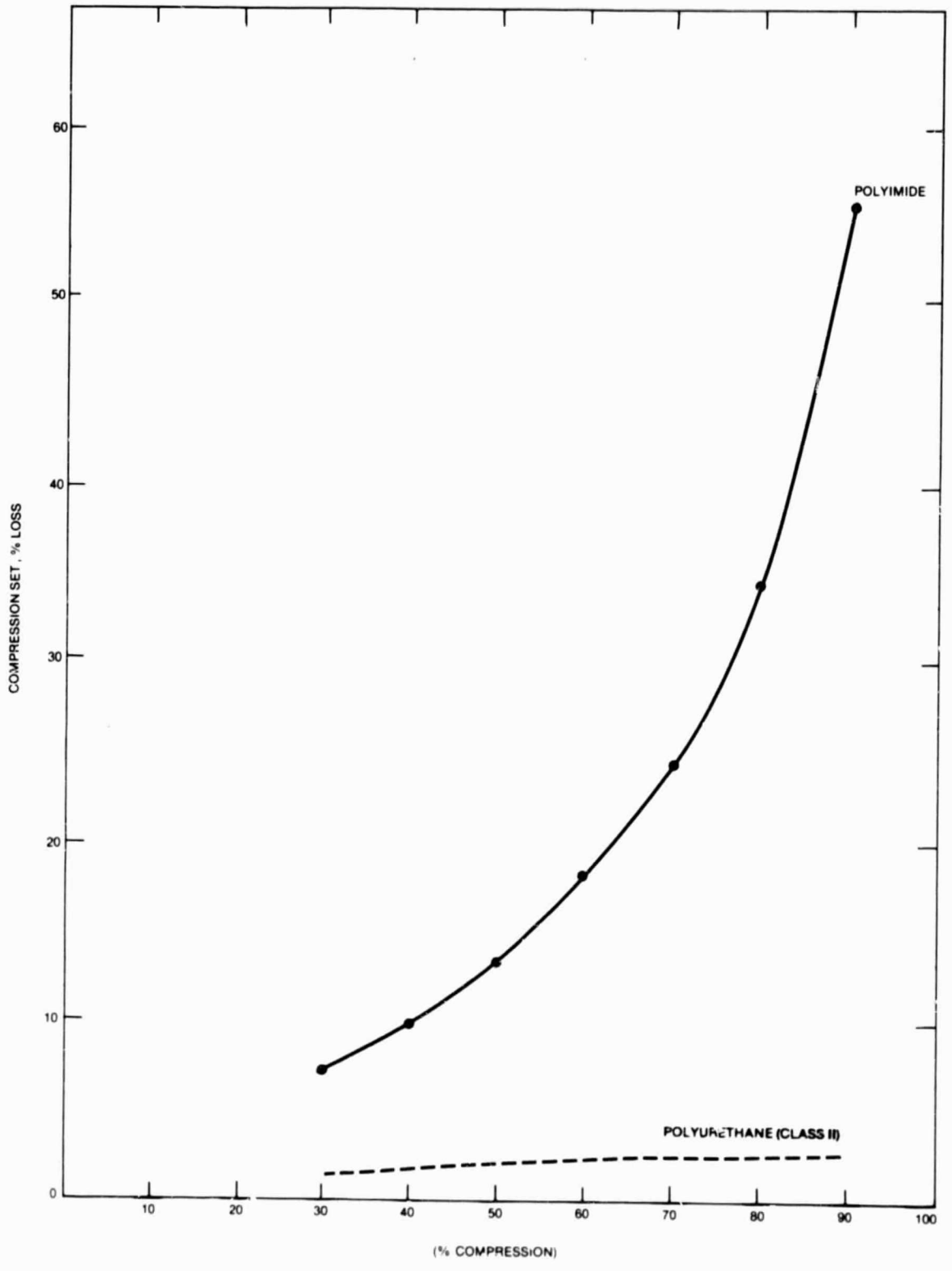


Figure 77. Compression Set Loss Values After 60 Minutes Recovery of Class II Polyurethane and Polyimide Foams at Specified Compressions

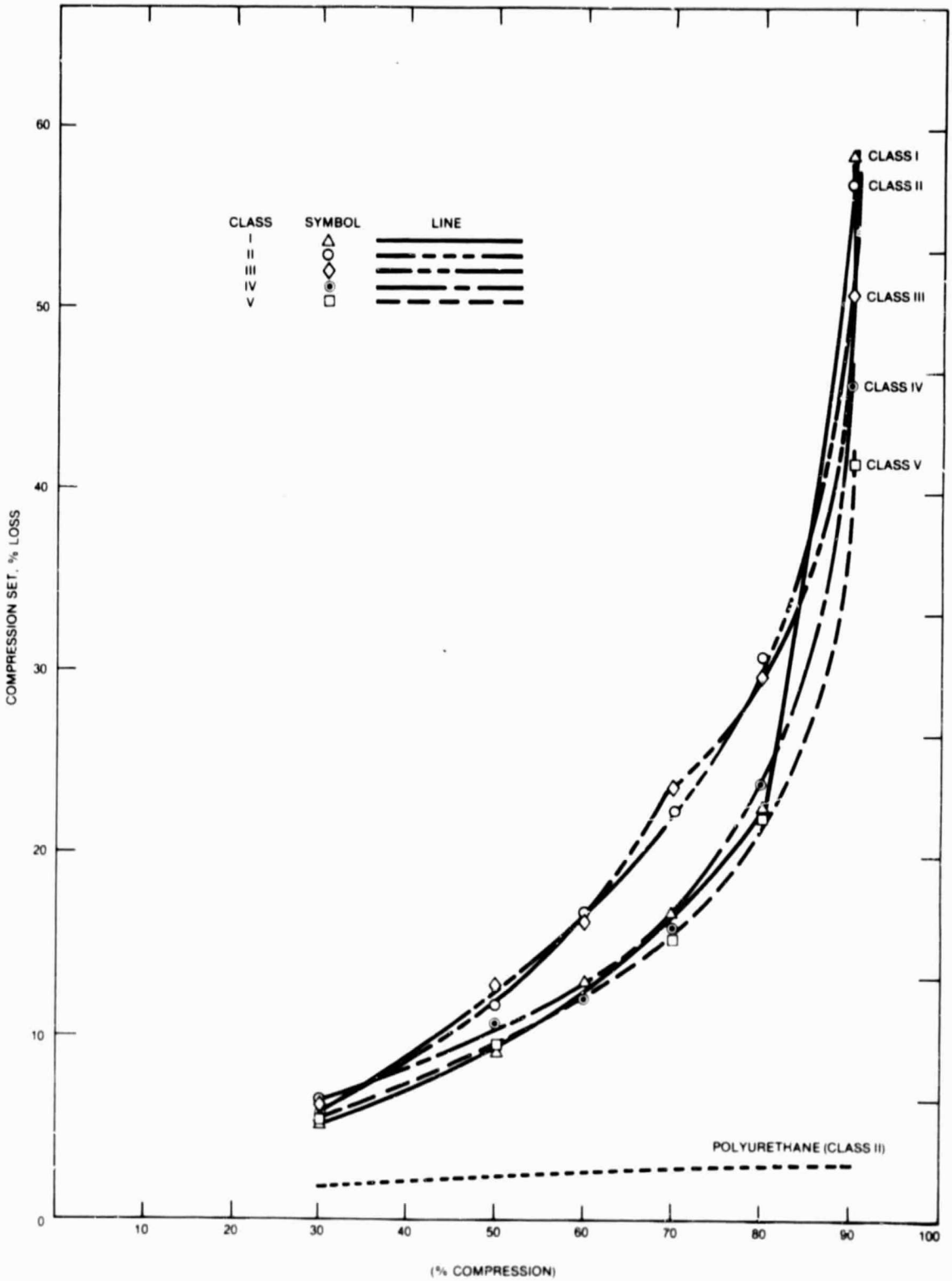


Figure 78. Compression Set Loss Values After 60 Minutes Recovery of Class II Polyurethane and Class I, II, III, IV, and V Polyimide Foams at Specified Compressions

state more readily and completely. The molecular structure of polyimide foams cannot be modified to increase their elastic properties without destroying the fire resistant characteristic of the material. Therefore, the compression set properties of these foams must be acccepted within these limitations.

The weight of a typical man (200 pounds) compresses polyimide foams between 60 and 70 percent as opposed to 80-90 percent for polyurethane foams as shown in Figure 75. This indicates that under service conditions polyimide foams will only be compressed to about 70 percent. Therefore, testing of polyimide foams to compression levels greater than 70 percent, where excessive force is required (see Fig. 75) is not realistic. The rate of recovery of polyimide foams is slower than for polyurethane as shown in Figure 75, therefore, this parameter must also be taken into consideration in evaluating the seating properties. Based on these considerations, the testing specifications of polyimide foams were modified. These modifications reflect the gross differences in molecular structure and are intended to be a reasonable and realistic evaluation of expected in-service performance of polyimide foams. The modifications are given in Table 42.

Table 42

Test Specifications for Seating Foams

Test	Current Specification for Polyurethane	Modified Specification for Polyimide
Compression Test	90% (<10% loss) 50% (< 5% loss) measured after 30 min.	70% (<25% loss) 30% (<10% loss) measured after 60 min.
ILD	25% 65%	25% 65%
Static Fatigue	75% measured after 30 min.	55% measured after 60 min.

4.4.3 Properties Evaluation

The selection of process parameters and compositions, as presented in Table 38, was done on the basis of data derived from the evaluation of functional properties of polyimide foams. In the selection criterion, ILD values, fatigue resistance, comfort index, compression set properties and density were given priority over other mechanical and physical properties of the foams. The rational behind this preference was dictated by the fact that polyimide foams have already shown to possess good thermal and mechanical properties as evidenced by tests reported in previous NASA-JSC sponsored

contractual efforts (Refs. 1, 2, and 3). The thermal and mechanical properties were evaluated in subsequent tasks for the purposes of developing final specifications for each class of foam as it will be reported in the next task.

4.4.4 Task IV - Polyimide Foam Evaluation and Classification - Summary

1. Powder precursors spray dried at an outlet temperature of 69 ± 1°C (156.2°F) produce foams falling within three of the five clases, specifically Class III, Class IV and Class V foams. This classification was achieved by variation of the blowing agent concentration.

2. The ILD values of polyimide foams at 25 percent deflection are directly proportional to the outlet temperature and inversely proportional to the concentration of blowing agent.

3. An outlet temperature condition of 69 ± 1°C (156.2°F) was selected. Foams produced from powder precursors dried at this temperature possess good fatigue properties, homogeneity within and between buns, and moderate compression set loss.

4. Combinations of blowing agent concentration, crushing technique, and spray drying temperature were employed to produce Class I and Class II foams.

5. Polyimide foams exhibit a very soft feel upon initial contact with the stress increasing progressively as the strain increases. In contrast, polyurethanes are initially quite firm, maintaining a near flat response to increasing strain up to 65 percent deflection.

6. Under service conditions, data indicate that polyimide foams will only compress to 60-70 percent of their initial height as opposed to 80-90 percent for polyurethane type foam. As a result, testing specifications for polyimide foams were modified to reflect this different behavior.

7. The process parameters and compositions used to produce all five classes of polyimide foams meeting the ILD requirements at 25 percent deflection in accordance with the program goal have been presented.

4.5 TASK V - PRODUCTS SELECTION AND SPECIFICATIONS

The objective of this task is to select at least one class of seating foam from each of the classifications defined by the value of 25 percent ILD to establish final product specifications.

To fully identify the characteristic and to establish minimum functional and performance requirements for each of the classes identified in this program, an extensive testing program was carried out for all physical, mechanical, and thermal properties in accordance with the program scope.

At the conclusion of this ta[illegible]. five foam classes were identified each representing a product and f[illegible] specification written for the NASA-JSC approval.

This task was carried out in three separate but complimentary subtasks as follows:

1. Data Evaluation

2. Selection of Classes

3. Specifications

4.5.1 Data Evaluation

This effort started with the fabrication of three sets of foams for each of the five classes of polyimide foam products in accordance with process parameters and compositions selected, and presented in Table 38. The foams were then evaluated for the most critical properties. Brief description of test methods of these properties follows:

Density. Density tests were performed in accordance with ASTM Designation D-3574-77, sections 6-12 inclusive.

Indentation Load Deflection at 25 and 65 Percent Indentation. The tests were performed in accordance with ASTM Designation D-3574-77, sections 12-18 inclusive.

Compression Set at 30 and 70 Percent Compression. The foams were tested in accordance with ASTM Designation D-3574-77, at 30 and 70 percent deflection.

Dynamic Fatigue. The foams were tested in accordance with ASTM Designation D-3574-77 by roller shear at constant force, sections 76-82 inclusive.

The three sets of foams were cut up in accordance with the schematic shown in Figure 42 to evaluate variation of properties within the bun.

Tables 43, 44, and 45 present the data generated from evaluation of sets No. 1, 2 and 3, respectively. These tables also show the selected process parameters employed. Table 46 presents the average of all data points for the three sets.

4.5.2 Selection of Classes

The process conditions and powder compositions employed in the effort of Task IV previously discussed have produced a method to rank polyimide foams into five classes in accordance with ILD values at 25 percent deflection. This

Table 43

Data Evaluation of All Five Classes, Set #1

Foam Number	527					526					525					528					529				
Concentration of Blowing Agent (%)	0.25					0.50					1.0					2.5					2.5				
Surfactant Concentration (%)	0.75					0.75					0.75					0.75					0.75				
Outlet Temperature (°C)	69 ± 1					69 ± 1					69 ± 1					69 ± 1					69 ± 1				
Curing Time (min.) Microwave Thermal	40.5 90					40 90					40 85					40 80					40 80				
Flexing	4 x (75%)					4 x (75%)					10 x (75%)					8 x (85%)					8 x (95%)				
	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)
	25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%	
1	59.7	296	16.3	7.7	1.18	41.0	162	34.2	10.6	0.90	41.0	167	36.0	10.3	0.95	29.4	111	23.7	8.8	0.85	21.3	87.0	24.3	7.9	1.06
2	59.7	278	35.6	8.4	1.17	45.0	188	38.1	9.8	0.97	40.0	168	36.2	9.5	1.02	26.3	101	32.1	8.3	0.98	18.2	73.4	23.9	8.5	1.01
3	90.1	344	19.5	6.8	1.47	56.7	219	28.6	8.4	1.10	55.7	207	25.7	9.3	1.16	41.0	148	20.5	8.4	0.98	27.3	90.1	20.1	8.2	0.99
4	85.5	298	18.7	7.0	1.38	59.2	215	22.2	7.1	1.06	53.6	195	22.1	7.5	1.05	36.2	130	20.5	7.8	0.91	24.0	81.0	20.2	7.9	0.94
5	82.0	314	20.3	6.5	1.53	46.1	[illegible]	23.9	7.1	1.16	48.6	195	22.2	8.3	1.06	35.9	149	33.5	9.6	0.92	28.8	110	23.3	7.4	1.24
6	74.4	283	16.9	6.6	1.31	51.6	153	18.9	6.7	1.24	53.1	223	19.6	7.2	1.08	36.9	156	21.8	7.8	0.89	32.6	124	19.5	7.2	1.22
Average	75.2	302	24.6	7.2	1.34	49.9	211	28.8	8.3	1.08	48.7	193	27.0	8.7	1.05	34.3	133	25.4	8.5	0.91	25.4	97	21.9	7.9	1.08
Fatigue Loss (%)	0.7					4.5					2.6					3.5					5.6				

Table 44

Data Evaluation of All Five Classes, Set #2

Foam Number	535					541					533					532					531				
Concentration of Blowing Agent (%)	0.25					0.50					1.0					2.5					2.5				
Surfactant Concentration (%)	0.75					0.75					0.75					0.75					0.75				
Outlet Temperature (°C)	69 ± 1					69 ± 1					69 ± 1					69 ± 1					69 ± 1				
Curing Time (min.) Microwave Thermal	40.5 90					40 90					40 85					40 80					40 80				
Flexing	4 x (75%)					4 x (75%)					10 x (75%)					8 x (85%)					8 x (95%)				
	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)
	25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%	
1	63.8	271	29.8	8.3	1.17	50.6	218	32.1	7.7	0.97	39.0	161.9	30.5	7.3	0.90	32.4	129.0	27.4	8.2	1.01	13.7	75.9	19.7	7.1	1.31
2	64.8	288	31.9	8.4	1.16	49.1	214	38.5	8.9	0.95	37.4	151.8	32.9	7.8	0.93	28.3	111.3	25.6	8.3	0.92	15.4	83.5	19.8	6.9	1.35
3	95.6	349	18.6	6.2	1.51	68.8	285	25.7	7.0	1.14	54.7	218.9	25.5	7.3	1.08	41.2	145.5	21.0	7.8	1.03	22.0	94.6	19.4	7.2	1.33
4	63.3	235	16.7	6.0	1.17	67.8	281	22.4	6.6	1.09	51.6	204.9	20.5	6.5	0.97	33.9	122.7	20.7	7.3	0.95	20.0	87.0	19.4	6.5	1.25
5	83.0	329	17.8	6.0	1.46	64.8	264	22.5	7.3	1.11	54.1	221.4	26.2	6.8	1.05	28.8	110.1	22.1	7.2	0.90	19.4	98.2	20.7	7.0	1.41
6	62.7	253	23.8	6.4	1.29	68.3	273	19.7	6.7	1.11	47.1	182.2	12.7	5.2	0.99	32.4	132.8	19.7	7.2	0.99	23.5	118.9	17.3	7.1	1.50
Average	72.2	288	22.6	6.9	1.29	61.6	256	26.8	7.4	1.06	47.3	190	24.7	6.8	0.97	32.8	125	22.8	7.7	0.97	19	93	19.4	7.0	1.36
Fatigue Loss (%)	1.4					2.1					2.6					7.5					6.9				

Table 45

Data Evaluation of All Five Classes, Set #3

Foam Number	540					539					538					537					536				
Concentration of Blowing Agent (%)	0.25					0.50					1.0					2.5					2.5				
Surfactant Concentration (%)	0.75					0.75					0.75					0.75					0.75				
Outlet Temperature (°C)	69 ± 1					69 ± 1					69 ± 1					69 ± 1					69 ± 1				
Curing Time (min.) Microwave Thermal	40.5 90					40 90					40 85					40 80					40 80				
Flexing	4 x (75%)					4 x (75%)					10 x (75%)					8 x (85%)					8 x (95%)				
	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)	ILD (lbf)		CS (%)		Density (lbs/ft^3)
	25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%		25%	65%	70%	30%	
1	78.4	377	27.5	7.4	1.28	50.6	215	28.6	7.1	1.05	41.5	172	26.8	7.2	1.00	28.1	109	25.1	7.6	0.89	17.7	86.5	19.5	6.6	1.24
2	57.7	250	33.4	8.7	1.04	50.1	215	33.8	8.5	1.07	42.5	182	33.3	7.9	1.00	25.8	97	22.4	6.9	0.92	18.2	86	20.7	6.5	1.24
3	68.3	258	29.5	8.4	1.16	72.4	283	23.7	5.7	1.32	57.2	230	19.5	6.7	1.13	36.9	138	18.1	6.2	0.99	27.8	99	19.0	6.8	1.20
4	72.9	293	27.[illegible]	8.7	1.22	62.7	240	17.9	6.9	1.17	54.7	221	21.4	6.1	1.[illegible]8	31.1	118	18.1	6.8	0.90	22.5	91	18.7	7.0	1.16
5	84.0	374	21.4	6.1	1.40	72.9	293	15.7	5.3	1.42	65.3	273	18.1	5.4	1.21	33.4	144	24.4	7.0	1.03	22.0	99	19.9	6.8	1.19
6	73.9	304	18.9	5.9	1.16	63.3	250	19.3	6.5	1.34	58.7	230	17.1	6.5	1.16	34.9	143	19.5	6.3	1.08	22.8	100	19.3	6.7	1.21
Average	72.[illegible]	309	26.4	7.5	1.21	62.0	249	23.2	6.7	1.1	5[illegible].8	218	22.7	6.6	1.1	31.7	125	21.3	6.8	0.97	21.8	94	19.5	6.7	1.21
Fatigue Loss (%)	0.7					2.7					1.51					5.9					3.4				

Table 46

Data Evaluation of All Five Classes

Class	I	II	III	IV	V
ILD, lbf					
25%	22.1	32.9	49.8	57.8	73.3
65%	95	128	200	239	300
Compression Set Loss (%)					
30%	7.2	7.3	7.4	7.5	7.0
70%	20.3	23.2	24.8	26.3	24.2
Density					
kg/m^3	19.5	15.2	16.7	17.9	20.5
lbs/ft^3	1.22	0.95	1.04	1.12	1.28
Fatigue Resistance					
Thickness Loss (%)					
8,000 cycles	5.3	5.6	2.2	3.1	0.9
20,000 cycles	31.7	21.0	16.3	19.2	1.3

same method has been used in the present task to fabricate three sets of foams for each of the five classes. The data derived from testing these sets have been found to be consistent with those previously developed as it was shown in Tables 43, 44 and 45.

Using these baseline data a final classification of the foams into five classes h s been successfully accomplished as shown below where the values of the ILD of the foams at 25 percent deflection represent the average for each of the classes. The final selected range for each of the five classes are also presented.

	ILD at 25% Deflection		
Classes	Program Goal	Actual Results	Selected Ranges
I	18	22.1	15-25
II	24	32.9	25-40
III	44	49.8	40-50
IV	50-55	57.8	50-60
V	70-80	73.3	70-80

With this effort the work to characterize, classify and select flexible resilient polyimide foams into five groups of products according to pre-established ILD values is concluded. Final product specifications are reported in the next subtask.

4.5.3 Specifications

The three sets produced in the preceding section were then evaluated for all physical, mechanical and thermal properties as set forth in the proposal. The data generated was used to establish final specifications for each of the five classes of polyimide foam products. The final specifications are reported in Table 47.

4.6 PRODUCTION OF PROTOTYPE SAMPLES

The end products of this contractual effort included sufficient slabs of resilient foams for fabrication of 15 single passenger seats. The dimensions of the slabs were 46.7 x 48 x 7.6 cm (18.5 x 18.9 x 3 in.) and 45.2 x 73.6 x 3.8 cm (17.8 x 29 x 1.5 in.). In addition a total of 600 board feet of foam were submitted for testing the five classes of foams for physical and mechanical properties.

These foams were produced using the process conditions selected in Task V and met the specification requirements established for each of the five classes.

Table 47

Specifications for All Five Classes of Polyimide Foams

Property	Test Method	Units	Class I	Class II	Class III	Class IV	Class V
Density	ASTM D-3574	lbs/ft^3 kg/m^3	1.1 - 1.3 17.6 - 20.8	0.9 - 1.1 14.4 - 17.6	0.9 - 1.1 14.4 - 17.6	0.9 - 1.1 14.4 - 17.6	1.1 - 1.3 17.6 - 20.8
ILD 25%	ASTM D-3574	lbf N	15 - 25 66.7 - 111.2	25 - 40 111.2 - 177.9	40 - 50 177.9 - 222.4	50 - 60 222.4 - 266.9	70 - 80 311.4 - 355.8
65%		lbf N	90 - 100 400 - 445	120 - 140 534 - 623	180 - 220 801 - 979	220 - 260 979 - 1156	280 - 320 1245 - 1423
Compression Set Loss (60 min. Recovery)	ASTM D-3574						
30%		%	10 max.	10 max.	10 max.	10 max.	10 max.
70%		%	25 max.	25 max.	25 max.	25 max.	25 max.
Tensile Strength	ASTM D-3574	psi N/m^2	15 min. $103x10^3$ min.	15 min. $103x10^3$ min.	15 min. $103x10^3$ min.	15 min. $103x10^3$ min.	15 min. $103x10^3$ min.
Elongation	ASTM D-3574	%	40 min.	40 min.	40 min.	40 min.	40 min .
Tear	ASTM D-3574	lbs/in. N/m	0.8 min. 140 min.	0.8 min. 140 min.	0.8 min. 140 min.	0.8 min. 140 min.	0.8 min. 140 min.
Resilience	ASTM D-3574	%	50 min.	50 min.	50 min.	50 min.	50 min.
Fatigue Resistance Dynamic	ASTM D-3574	% loss in thickness					
8,000 cycles			7 max.	7 max.	7 max.	7 max.	7 max.
20,000 cycles			25 max.	25 max.	25 max.	25 max.	25 max.
Static (55% compression) (60 min. Recovery)		% loss in thickness	12 max.	12 max.	12 max.	12 max.	12 max.
Hydrolytic Stability	74°C, 100% RH, 7 days	% loss in ILD	5 max.	5 max.	5 max.	5 max.	5 max.
Odor			ND*	ND	ND	ND	ND
Oxygen Index	ASTM D-2863	%	38 min.	38 min.	38 min.	38 min.	38 min.
Smoke Density	NBS		5 max.	5 max.	5 max.	5 max.	5 max.
Thermal Stability	Thermogram	Loss at 204°C (400°F)	None	None	None	None	None

*ND = not detectable

5

RECOMMENDATIONS FOR FUTURE WORK

At the present state of development polyimide foams have been classified into five different products, each possessing specific ILD values which have been produced in large scale pilot plant size. These foams have been made by microwave processing using an open mold to overcome the problems of collapsing experienced with free-rise techniques. The finished foam slabs are then cut from the large buns for fabrication of the finished seat cushions. Two problems have been encountered utilizing this cutting technique which are (1) high scrap rate and (2) variation of foam properties within the bun itself. Although the variation of properties is significantly low at the present pilot plant stage, it is expected to increase as the process is further scaled-up.

These problems will be overcome and the product significantly improved by developing compositions and procesess for molding the resilient foams to specific sizes and shapes as required by the aircraft seat manufacturers. The advantage of this method are low foam scrap and superior wear properties due to the surface skin resulting from the molding operation. This skin is flexible, tough and impermeable to liquids and could be considered as a possible replacement for the standard ticking.

The same process with minor modifications of the resin composition can also be utilized to produce light weight rigid foams of specific shapes for use as ducting, pipes, decorative paneling, galley modules, storage compartments and others.

This technology once fully developed will be expanded to produce a variety of low density foam products to replace more flammable components used in aircraft and spacecraft applications.

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